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ATMOSPHERIC EMISSIONS FROM HYDROCHLORIC ACID MANUFACTURING PROCESSES

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ATMOSPHERIC EMISSIONS FROM HYDROCHLORIC ACID MANUFACTURING PROCESSES

Cooperative Study Project
Manufacturing Chemists' Association, Inc.
and
Public Health Service

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Consumer Protection and Environmental Health Service
National Air Pollution Control Administration
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PREFACE

To provide reliable information on the nature and quantity of emissions to the atmosphere from chemical manufacturing, the Public Health Service, United States Department of Health, Education, and Welfare, and the Manufacturing Chemists' Association, Inc., entered into an agreement October 29, 1962, to study emissions from selected chemical manufacturing processes and to publish information that would be helpful to air pollution control and planning agencies and to chemical industry management.* Direction of these studies is vested in an MCA-PHS Steering Committee, presently constituted as follows:

Representing PHS	Representing MCA
Stanley T. Cuffe†	Willard F. Bixby†
Robert L. Harris, Jr.	Louis W. Roznoy
Dario R. Monti	Clifton R. Walbridge
Raymond Smith	Elmer P. Wheeler

Information included in these reports describes the range of emissions during normal operating conditions and the performance of established methods and devices employed to limit and control such emissions. Interpretation of emission values in terms of ground-level concentrations and assessment of potential effects produced by the emissions are both outside the scope of this program.

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*Reports in this series to date are *Atmospheric Emissions from Sulfuric Acid Manufacturing Processes*, Public Health Service Publication No. 999-AP-13; *Atmospheric Emissions from Nitric Acid Manufacturing Processes*, Public Health Service Publication No. 999-AP-27; and *Atmospheric Emissions from Thermal-Process Phosphoric Acid Manufacture*, National Air Pollution Control Administration Publication No. 48. These publications are available from the Manufacturing Chemists' Association, Washington, D.C., and the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

†Principal representatives.

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Samuel L. Bean of Allied Chemical Corporation, Industrial Chemicals Division, and Howard Wall, Jr., National Air Pollution Control Administration, were the investigators in the study and are the authors of this report. The sponsors acknowledge the contribution of the Allied Chemical Corporation in providing the services of Mr. Bean.

USE AND LIMITATIONS OF THIS REPORT

This report is one of a series on atmospheric emissions from chemical manufacturing processes. It provides such information on the manufacture of hydrochloric acid. Basic characteristics of the industry, including growth rate, manufacturing processes, product uses, and the number of producing plants in the United States are discussed. Process descriptions are given for the chlorinated by-product process and the synthesis process, which employs the direct combustion of hydrogen in chlorine. Mannheim, Hargreaves, and several other processes are included for their historical interest, even though the number of plants that use them is decreasing rapidly. Process information includes the range of emissions of hydrogen chloride from hydrochloric acid manufacturing plants and the methods of limiting or controlling these emissions to the atmosphere. Although other contaminants such as chlorine, chlorinated organics, and other hydrocarbons emitted to the atmosphere from these plants are mentioned and in some cases discussed, they are not the primary concern of this report. Detailed descriptions of the sampling and analytical methods used in measuring such emissions are also included.

The production of hydrochloric acid has been a basic industry in the United States for many years; manufacturing procedures have become well established. Plant design, throughput rates, and the use of special systems to reduce emissions are factors that influence atmospheric emissions.

Emission data contained in this report were obtained from 18 percent of the present hydrochloric acid manufacturing locations. Most of the data are from the records of acid producers. The data include results of stack sampling programs conducted by the National Air Pollution Control Administration as part of the joint study.

Although this report is a technical review prepared primarily for public officials concerned with the control of air pollution, it is expected that it will also be helpful to chemical plant management and its technical staff. This report should be reviewed at intervals to determine when revision is necessary to reflect prevailing conditions.

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ATMOSPHERIC EMISSIONS FROM HYDROCHLORIC ACID MANUFACTURING PROCESSES

SUMMARY

MANUFACTURING PROCESSES

Approximately 80 percent of the hydrochloric acid in the United States is manufactured as a by-product of the chlorination of organic compounds. By-product hydrogen chloride is produced in the manufacture of chlorinated benzene, vinyl chloride, chlorinated methane, chlorinated ethylene, toluene diisocyanate, and other such compounds.

The second most important source of hydrochloric acid is the synthesis process in which hydrogen is reacted with chlorine. This process produces a relatively pure hydrogen chloride, which may be converted to hydrochloric acid or recovered as anhydrous hydrogen chloride.

Less than 10 percent of the hydrogen chloride manufactured in the United States is produced by a reaction of sulfuric acid on metal chlorides, the principal one of which is sodium chloride. Table 1 illustrates the decline in importance of the salt process and the increased importance of by-product hydrogen chloride sources.

Table 1. PRODUCTION OF HYDROCHLORIC ACID BY PROCESS TYPE (percent of total)[1]

Year	Salt reaction	Synthesis	By-product
1935	86	14	–
1947	53	4	43
1958	13	18	69
1961	10	13	77
1962	9	14	77
1966	9	7	84
1967	8.5	7	84.5

Hydrogen chloride is often processed into hydrochloric acid in package plants that consist of a falling film absorber and a packed tower. If the unit is

used to make acid from a by-product process, the organic materials are usually removed from the hydrogen chloride by condensation or absorption before the hydrogen chloride is absorbed in water.

If the organic content of the acid is objectionable, another kind of package plant, which consists of an adiabatic unit in which the acid is formed at its boiling point in a packed column, may be used. In this case, organic materials with low boiling points are not allowed to condense. The acid is then cooled and passed through a carbon bed to remove the final traces of organic material

Regardless of the type of hydrogen chloride absorber used to form hydrochloric acid, the most efficient system, from an atmospheric emission viewpoint, is characterized by a final scrubber that removes any remaining trace of hydrogen chloride from the system.

HYDROCHLORIC ACID PRODUCTION

In 1965 a total of 1,318,122 tons of hydrochloric acid was produced in the United States.[1] Based on the increase in production between 1945 and 1965, the growth rate is 40,000 tons per year, as shown in Figure 1.

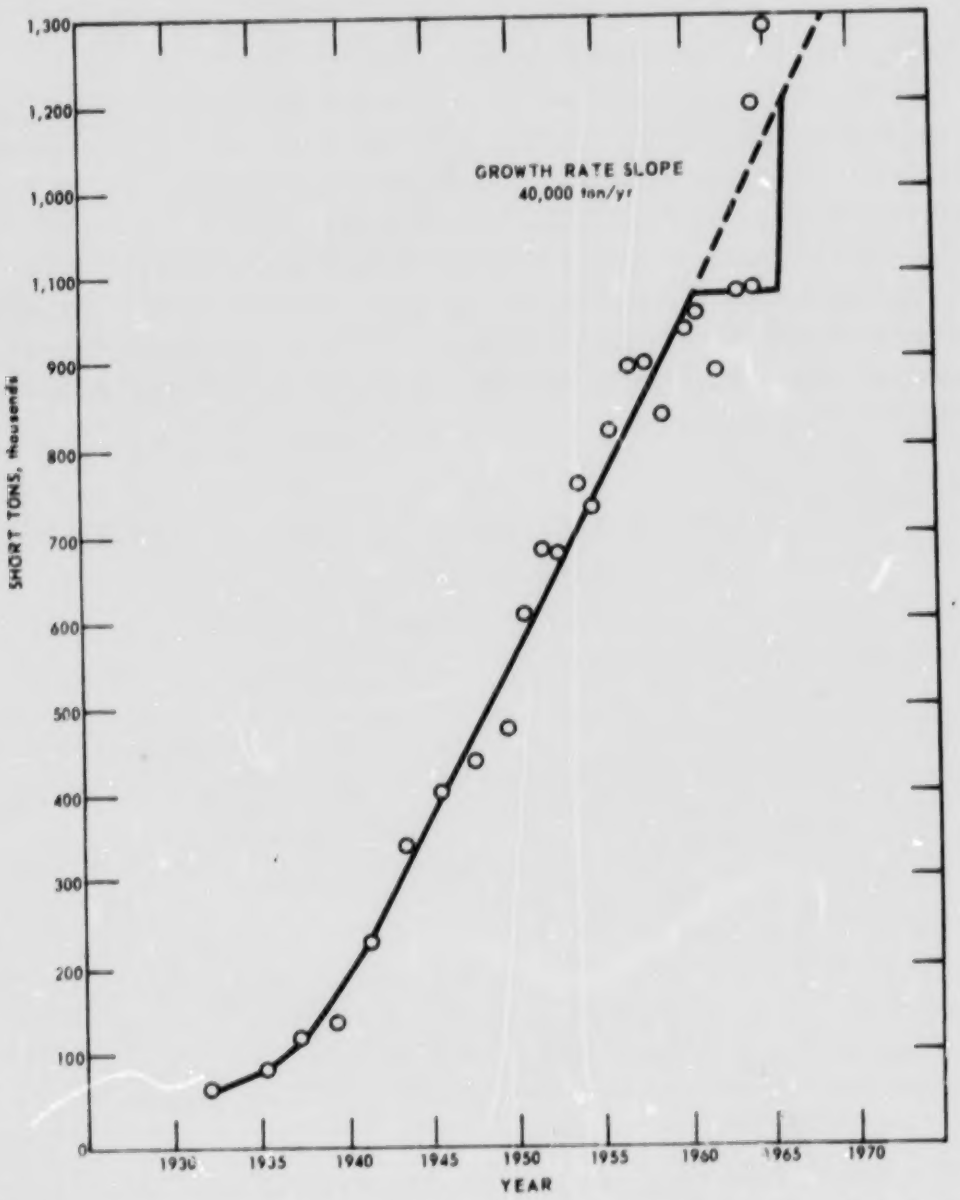


Figure 1. Yearly production of 100 percent hydrochloric acid.

TYPICAL EMISSIONS

The atmospheric contaminants emitted from the manufacture of hydrochloric acid are hydrogen chloride, chlorine, chlorinated organic compounds, and other organic materials. The exact type and quantity of contaminants vary with the process and the type of tail gas control system used.

The concentration of hydrogen chloride emitted to the atmosphere is usually less than 0.5 percent of the tail gas volume emitted to the atmosphere. The average tail gas volume emitted to the atmosphere from the plants reviewed for this report is 40 cubic feet per minute, with the rates ranging from 2 to 550 cubic feet per minute.

On a combined basis, the tables herein show that 6 of the 26 plants reporting were emitting hydrogen chloride above the 0.5 percent level. One of the six plants was permanently shut down after testing. Another was in the process of installing a new scrubber to reduce emissions to the 0.5 percent level. Another dispersed its gases by diluting them with stack gases from a boiler.

CONTROL OF EMISSIONS

Emissions from hydrochloric acid plants are adversely affected by (1) high temperatures in the absorption system, (2) improper balance of absorption area and contact time, (3) faulty equipment, and (4) inadequate tail gas scrubbing systems. Emissions of hydrogen chloride or hydrochloric acid can also be caused by operational upsets.

The most common method used to remove hydrogen chloride from tail gas is to scrub the gas with water. This method is inexpensive and effective. Alkaline scrubbing is sometimes used when other compounds that are not readily absorbed in water, such as chlorine or phosgene, are present.

Emissions of organic and chlorinated organic compounds, which come from sources other than the direct manufacture of hydrogen chloride or hydrochloric acid, vary considerably and present a different problem in each case. Reduction of emissions of these compounds may require a more efficient organic absorption system, a phosgene breaker, a benzol absorption system, or some other system especially suited to remove a particular emission. Efficiencies of these control systems often exceed 99 percent.

In some cases, emissions to the atmosphere are prevented by utilizing a closed system for the entire organic and hydrogen chloride plant.

EMISSION GUIDELINES

Hydrogen chloride emissions to the atmosphere usually total less than 0.5 percent of the tail gas volume. This is a relatively small quantity of hydrogen chloride because gas volumes for plants reporting range from 2 to 550 cubic feet per minute with an average of 40 cubic feet per minute.

Adequate control equipment is available to prevent emissions of more than 0.5 percent hydrogen chloride, or about 0.5 pound per ton of acid produced.

In the event of an emergency shutdown of a hydrochloric acid plant, the hydrogen chloride gas source should be shut down first. Liquid flow to absorption equipment should be maintained at a level sufficient to keep all

tubes and/or packing wetted and thus prevent hydrogen chloride emissions to the atmosphere. Some weak acid will be made during this shutdown period, but it can usually be adjusted by producing somewhat higher-than-normal-strength material later. This technique of maintaining at all times more liquid flow than the amount required for surface wetting should also be used to prevent hydrogen chloride emissions during routine shutdowns and startups.

GROWTH OF HYDROCHLORIC ACID MANUFACTURING INDUSTRY

HISTORICAL BACKGROUND

Hydrochloric acid, which is also called muriatic acid, was first described by Valentius in the Fifteenth Century and was studied by such eminent chemists as Thenard, Cavendish, Priestly, and Gay-Lussac.[2] The first large-scale production of hydrogen chloride began as a by-product in the LeBlanc soda ash process wherein salt and sulfuric acid are reacted to produce salt cake. Originally this hydrogen chloride gas was vented to the atmosphere; however, since this indiscriminate discharge killed vegetation over a large area surrounding the manufacturing plants, legislation was soon introduced in England to prohibit it. This restriction initiated the expedient of dissolving the hydrogen chloride in water, which forms hydrochloric acid. Soon uses were discovered for the acid, and subsequently plants were built for its manufacture as the primary product with salt cake as a by-product. Demand for salt cake was reduced as the Solvay process replaced the LeBlanc process for making soda ash.

In the United States, the reaction of sulfuric acid and salt, an initial step in the LeBlanc process, was used to manufacture hydrochloric acid rather than soda ash as the prime product. The heating of salt and sulfuric acid to form hydrogen chloride gas is also the principal operation of the Laury and the Mannheim processes. The Hargreaves process, which involves reaction of salt and sulfur dioxide, is used in only two plants in the United States; and like the Mannheim process, it is costly and its use probably will be discontinued soon.

As can be seen in Table 1, originally, most hydrochloric acid was produced from the reaction of salt and sulfuric acid. As the chemical industry grew, more acid was produced through by-product methods and more acid was produced by burning hydrogen in chlorine than was produced from the reaction of salt and sulfuric acid. At the present time, the by-product process is the largest source of acid; burning of hydrogen in chlorine (synthesis process), the second largest source; and salt - sulfuric acid and other processes, the third largest source of acid. Table 2 and Figure 1 show the growth trends of this industry.

CURRENT USES

Because a large portion of the total hydrochloric acid produced is derived from by-product operations, the locations of production do not always coincide with the areas of use. Shipping costs for acid are high because about 70 percent by weight of the usual commercial-strength acid is water. Unusual regional supply-and-demand situations result. In some localities a Mannheim furnace, which is usually costly to operate, can be run at a profit to produce acid for local needs. At other locations (along the east coast of the United States in particular) by-product acid is often in oversupply and is dumped into the ocean. Some manufacturers ship hydrogen chloride in its anhydrous liquid

form to reduce transportation costs and to enable them to compete in markets far from the source of production.

Table 2. HYDROCHLORIC ACID PRODUCTION IN UNITED STATES[1]

Year	Tons HCl produced 100 % basis
1933	63,000
1935	87,000
1937	122,000
1939	140,000
1941	228,000
1943	342,000
1945	408,000
1947	442,558
1949	484,000
1950	618,784
1951	693,541
1952	683,742
1953	771,241
1954	740,604
1955	838,249
1956	911,430
1957	917,081
1958	848,487
1959	955,914
1960	970,167
1961	910,967
1962	1,052,116
1963	1,079,443
1964	1,228,068
1965	1,368,122
1966 (preliminary)	1,505,000
1967 (preliminary)	1,597,000

Hydrochloric acid is used for pickling steel, for producing glucose from corn and other starches, making and purifying bone char, bleaching sugar, chlorinating chemical compounds, chlorinating rubber, activating petroleum wells, and processing food and drugs.

Less well known uses include the manufacture of alkyl chloride used in making tetraethyl lead; preparation of chlorides from alcohols; preparation of pharmaceutical-grade chemicals such as adipic acid, citric acid, amine hydrochlorides, and aconitic acid; dehairing of skins in tanning; and production of silica gel. Hydrochloric acid is also used as a catalyst in organic reactions.

Several recently built vinyl chloride plants both make and use hydrochloric

acid.[3,4] Part of such a plant manufactures vinyl chloride with chlorine, which yields the by-product hydrochloric acid. The other part of this plant manufactures vinyl chloride utilizing the by-product hydrogen chloride. Such a plant can be designed and operated so that no excess acid is produced.

HYDROCHLORIC ACID MANUFACTURING PROCESSES

BY-PRODUCT HYDROGEN CHLORIDE

By-product hydrogen chloride, which results from the chlorination of organic compounds, constitutes the largest source of hydrochloric acid. Numerous reactions will form hydrogen chloride. Most of these reactions take place when chlorine is added to an organic compound. If a chlorinated hydrocarbon is hydrolized with water, hydrogen chloride is produced. An example of a process that generates hydrochloric acid as a by-product is the direct chlorination of benzene. The equation for the chlorination of benzene is:

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$$

This reaction takes place in the presence of a chlorine carrier, such as ferric chloride.[2] The yield is about 70 percent. In addition to the conversion of benzene to benzene monochloride, some benzene dichlorides are formed according to the reaction:

$$C_6H_5Cl + Cl_2 \longrightarrow C_6H_4Cl_2 + HCl$$

Benzene dichloride concentration can be increased by allowing the monochloride to remain in the reactor for a longer period of time than required for its production. The ratio of paradichlorobenzene formed to orthodichlorobenzene is generally fixed, but trace additives can be used in the chlorine to vary this ratio.

Chlorobenzenes are used as intermediates for synthesizing various organic compounds, solvents and preservatives for paints, moth balls, fumigants, germicides, and deodorants.[2]

Hydrogen chloride is formed also by regeneration in some chlorination processes. For example, the chlorination of benzene and subsequent hydrolysis to phenol occur according to the following reactions:

$$2C_6H_6 + 2HCl + O_2 \longrightarrow 2C_6H_5Cl + 2H_2O$$

$$C_6H_6Cl + H_2O \longrightarrow C_6H_5OH + HCl$$

In such reactions, the chlorination and hydrolysis take place in separate steps and the acid is separated, purified, and sent back to the chlorination process.

Other processes that produce hydrogen chloride include the chlorination of methane, the chlorination of paraffin, and the formation of intermediates for urethane foams.

TYPICAL PROCESS DESCRIPTION - CHLOROBENZENE

The raw materials required for making chlorobenzene are benzene, chlorine, hydrogen, air, and some trace catalysts for special reactions.

Benzene used is either moisture free or is dried with sodium hydroxide before being introduced into the reaction. The chlorine is also moisture free. Before chlorine is introduced to the benzene, 1 to 3 percent hydrogen is added along with sufficient air to reduce the chlorine concentration to between 80 and 85 percent. As shown in Figure 2, the benzene and chlorine streams are fed into tanks containing iron rods. These rods act as a chlorine carrier by forming ferric chloride. Because the reaction is exothermic, a portion of the chlorinated benzene mixture is cooled in a heat exchanger and returned to the reactor. Cooling controls the rate of reaction.

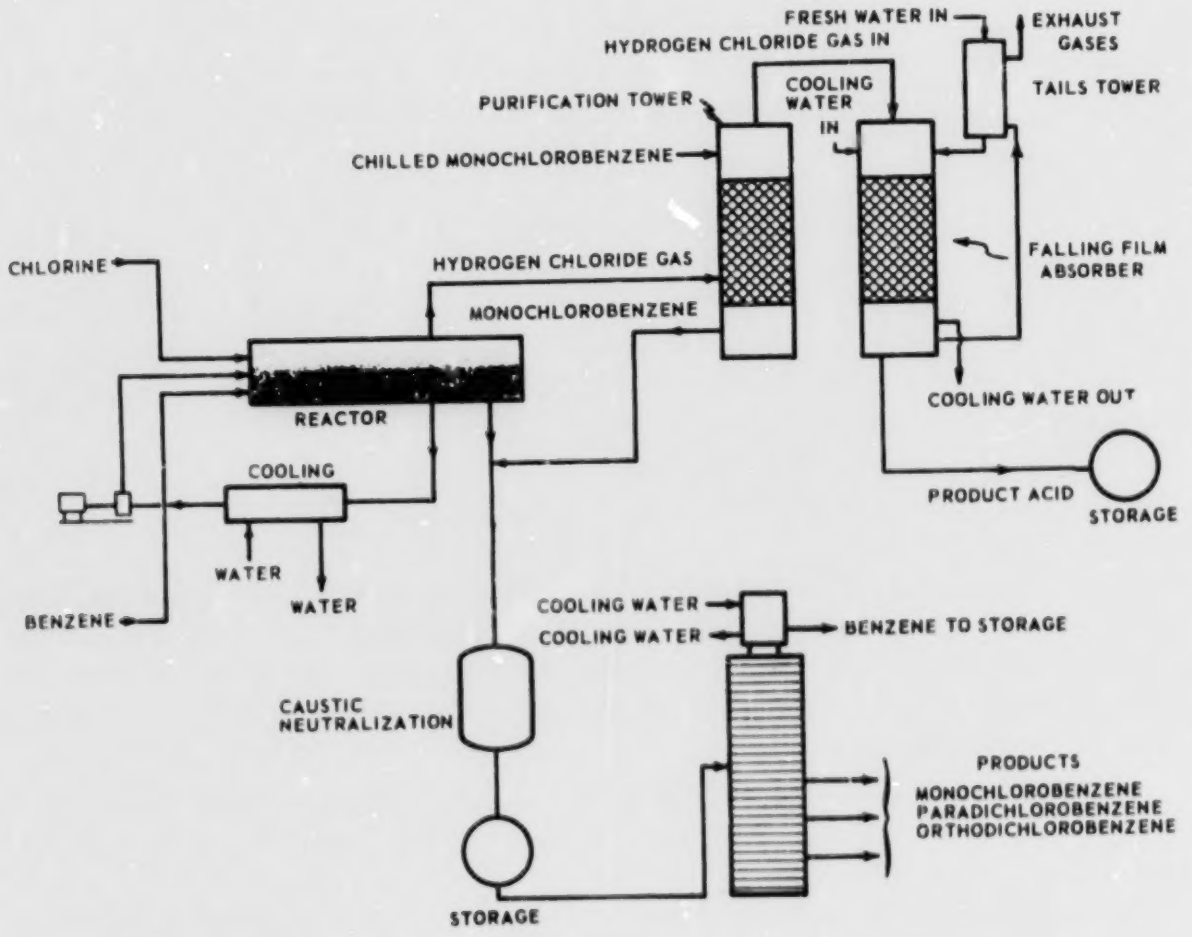


Figure 2. Typical by-product hydrochloric acid process (chlorobenzene).

The liquid components of the reaction are chlorobenzenes and benzene. The gases from the reactor consist of hydrogen chloride, benzene, chlorobenzenes, and air.

Product liquid is neutralized with sodium hydroxide and separated into constituents by fractionation. Any separated benzene is returned as process feed. Gases leaving the reactor are processed to recover benzene, chlorobenzenes, and hydrogen chloride gas. These gases are first scrubbed in a

packed tower with a chilled mixture of monochlorobenzene and dichlorobenzene to condense and recover any benzene or chlorobenzene. The hydrogen chloride is then absorbed in a falling film absorption plant as described in the section on absorption systems. The chlorobenzene scrubbing liquid is recycled to the main reaction vessel.

EMISSIONS

Hydrogen chloride emission data, in addition to data on other trace emissions from by-product plants, are presented in Table 3. Most of the plants contacted by questionnaire (Plants Number 1 through 17) indicated no emissions of hydrogen chloride. However, further investigation indicated that a value of 0.5 percent hydrogen chloride by volume in the exit gas is considered by most plants to be negligible and is therefore reported as zero. Two of the four plants tested by the PHS sampling team (Plants Number 18 through 21), however, showed results somewhat higher than the reporting plants. To ensure more accurate results, greater effort was expended by the sampling team in making these tests than would normally be used in making routine analyses.

Concentration of hydrogen chloride in the emissions to the atmosphere range from 0 to 50.6 percent by volume. Because of the diverse methods of production, no correlation exists between exit gas volumes and plant production rates. However, smaller volumes of exit gas usually show greater hydrogen chloride concentrations. This variation in concentration in exit gas is partly due to the varying amounts of inert materials in this gas stream. For this reason the amount of hydrogen chloride emitted in pounds per ton of acid produced gives a more accurate picture of the contaminant emissions. On this basis emissions range from 0 to 8.5 pounds of hydrogen chloride per ton of actual acid produced.

In plant BP-19, where the 8.5 value was recorded, the hydrogen chloride was emitted during a period of about 30 minutes of a 4-hour test period. This particular plant was arranged so that two separate chlorination units were connected to one acid plant. In this test one unit was turned on too rapidly and hydrogen chloride was blown out of the absorption plant until the unit could be stabilized. This represents an example of improper operation because this unit could have been turned on gradually and the hydrogen chloride emitted to the atmosphere would have remained in the range of 0.16 to 0.24 pound per ton as it was in the two 1-hour tests that followed.

Plant BP-21 emitted about 2.6 pounds of hydrogen chloride per ton of acid produced. This plant was not equipped with a final scrubber, a fact which partially accounts for the higher hydrogen chloride emission rate. However, mixing this gas with the exhaust gases from a 1,000,000-Btu-per-hour boiler dilutes the emissions to the atmosphere.

A hydrogen chloride emission concentration of 0.5 percent at an exit gas flow rate of 40 cubic feet per minute will result in an emission rate of about 1.2 pounds of hydrogen chloride per hour.

CONTROL OF HYDROGEN CHLORIDE EMISSIONS

Tail gas concentrations of contaminants emitted from a typical by-product plant are often reduced by scrubbing in a packed tower located behind the

Table 3. EMISSIONS FROM BY-PRODUCT HYDROCHLORIC ACID MANUFACTURING PLANTS

Plant number	Plant capacity, tons per day	Acid concentration, ° Bé	Exit gas conditions		Percent HCl[a]	Control equipment	Substances other than HCl entering atmosphere	Pounds HCl emitted per ton of 20° Bé acid produced[b]
			Volume, cfm	Temperature, ° F				
BP-1	115	20	200	180	0	Water jets on storage tanks	Air, hydrogen, carbon monoxide and dioxide	None
BP-2	40	20	0	60	NA	Water scrubber	Trace inerts	None
BP-3	30	20	0	NA	NA	None	NA	None
BP-4	15	20	NA	NA	NA	Caustic scrubber	NA	None
BP-5	220	20	2	100	0	None	Air, carbon dioxide	None
		22						None
BP-6	70	20	180	50	0	None	Air, benzol	None
BP-7	15	22	NA	NA	0	None	None	None
BP-8	7	22	0	85	0	Water scrubber back up	None	None
BP-9	76	20	270	104	NA	Phosgene decomposition towers	Nitrogen and Phosgene	None
BP-10	12	20	NA	NA	NA	None	NA	None
BP-11	25	20	0.01	60	0.01	None	Water vapor	None
BP-12	30	20	Leakage only	85	NA	Fume jet	Chlorine	None
BP-13	30	20	10	100	3	None	Air, organics	1
BP-14	105	22	315[c]	70	0	Closed system	Methane, nitrogen, R Cl	None
BP-15	141.5	22	138[c]	70	0	Closed system	Chlorine, R Cl	None
BP-16	17.8	22	NA	70	0	None	Inerts	None
BP-17	8.3	20	0.1-3.5	108	0	Na_2CO_3 scrubber	Chlorine	None
BP-18[b]	90	20	520	75	<0.001	Caustic scrubber	Nitrogen, traces of aromatics	<0.008
BP-19[b]	60	20	187	57	0.024	Water scrubber	NA	0.10
					0.160			0.70
BP-20[b]	140	20	187	40	1.95	Water scrubber	Organics	8.5
					0.0023			0.0044
					0.0019			0.0037
BP-21[b]	225	20	8.3	50	0.0745	None for HCl, CCl_4 scrubber for chlorine	Chlorine, carbon dioxide	0.14
					50.6			2.6
					47.2			
					53.9			2.5

NA not available.

[a]Represents 0.5 percent HCl or less.

[b]Tested by PHS sampling team.

[c]Recycled--closed system.

final process tower. Venturi scrubbers are also used occasionally. If hydrogen chloride is the only component to be removed, water is universally used as the scrubbing agent. As shown in Table 3, water scrubbers can reduce hydrogen chloride concentration to less than 0.1 pound of HCl emitted per ton of acid produced. Alkaline scrubbing is sometimes employed when the gases contain substances like chlorine or phosgene, which are not readily absorbed in water.

Removal of organic materials from exhaust gases poses a separate design problem for each specific compound. If phosgene is present, a decomposition system is needed. If benzene or phenol is present, scrubbing with a solvent is necessary. In some cases use of the proper scrubbing solution will efficiently remove all of the organic compounds present.

Some plants use a completely closed system from which there is no continuous emission of exhaust gases to the atmosphere.

By-product hydrogen chloride plants, by their nature, are adjuncts to other processes; therefore, they may be affected by upsets that occur in the process in which the hydrogen chloride is evolved. Good controls and secondary scrubbing systems can reduce the possibility of increasing emissions resulting from such upsets.

SYNTHESIS PROCESS

Introduction

High-purity concentrated hydrogen chloride may be synthesized by burning hydrogen in chlorine, as shown in Figures 3 and 4. High purity is desirable for organic compound or drug synthesis and in the manufacture of reagent-grade acid.

Hydrogen chloride is made in accordance with the equation:

$$H_2 + Cl_2 \longrightarrow 2\ HCl$$

The source of chlorine is usually chlorine cell gas, although waste chlorine (blow gas) can be used. Hydrogen can come from any source of relatively pure hydrogen, but usually it is from the electrolysis of brine or steam reforming of a relatively pure organic compound.

The purity of the raw materials determines the purity of the product. Chlorine usually contains some organic materials and oxygen in addition to water that can result in water vapor within the combustion chamber. Hydrogen may also contain water vapor and organic compounds. The net result of water vapor in the feed gases is that it can condense in the combustion chamber and form hydrochloric acid. This may cause corrosion unless impervious graphite materials are used in the combustion chamber.

A typical product will contain 0.5 percent hydrogen, 0.1 percent water vapor, 0.1 to 1.5 percent inerts, and the balance hydrogen chloride. In addition, some carbon dioxide may be present.

A slight excess of hydrogen is used in this process, and this assures a chlorine-free product. Combustion takes place in a closed chamber under a slight positive or slight negative pressure, depending on chamber type. A burner, shown in Figure 4, injects the chlorine into a surrounding hydrogen

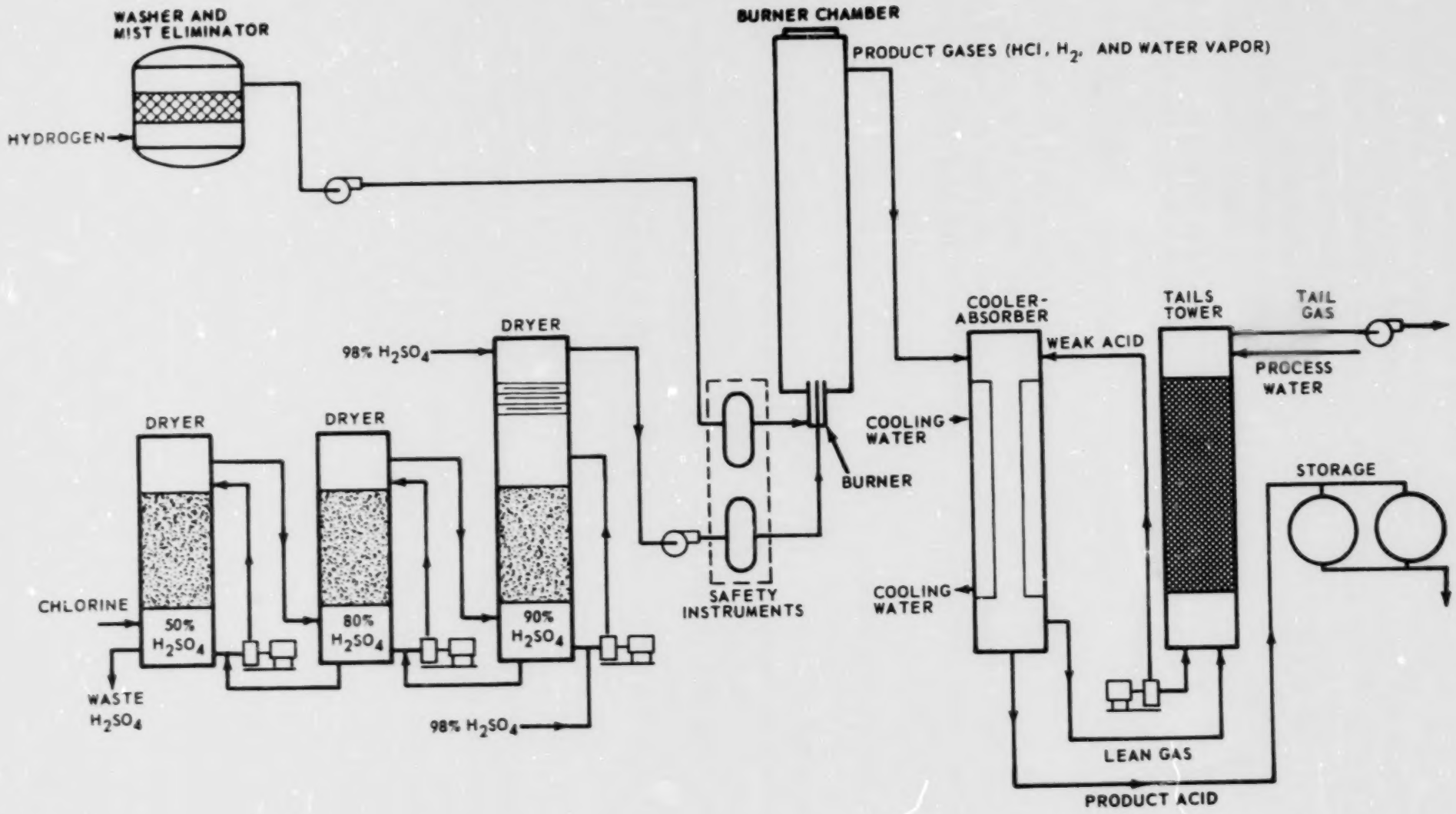


Figure 3. Synthesis chlorine-hydrogen process.

stream. The original ignition is initiated by using a retractable air-hydrogen torch or an electrical ignition device.

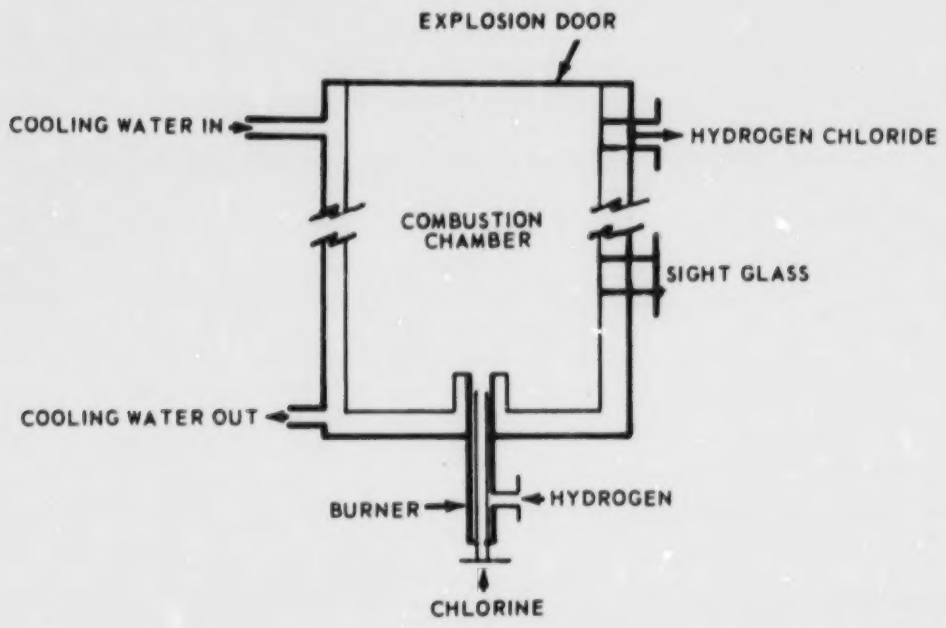


Figure 4. Synthesis process hydrogen-chloride burner.

Synthesis plants differ in detail because of differences in raw material sources and qualities, and plant capacity. However, all plants consist of a chlorine burner, including control and safety devices, and acid purifying and absorption facilities. Burners may be steel with a silica or brick lining, water-jacketed steel, or water-cooled graphite. Brick burners are commonly used, especially for large units, but they have the disadvantage of a high product temperature, i.e., about 2,200° F. Water-jacketed steel is good if the temperature of the jacket is maintained above the dew point of the materials within the burner. The outlet temperature from a water-cooled burner is within a range of 700° to 1,000° F.

A burner consists of one or more nozzles, which inject the gases into the combustion chamber, and can have a range of capacity of 8 to 16 tons of hydrogen chloride per day. Control of the gas burner may be manual or automatic. The trend presently is toward automatic operation.

Controls include safety devices and purge systems. Burner chambers have an explosion rupture disc to protect the vessel and surrounding area. The inlet gas lines are provided with automatic shutoff valves and seals to prevent back flow of reactants due to reports. An ignition device is sometimes included in the outlet duct to prevent the delivery of an explosive mixture of gases instead of hydrogen chloride. Other control and safety devices include flame sensors; temperature-regulated controls for various purposes; and a purge system, which usually injects carbon dioxide, that operates automatically in case of an interruption in any of the services.

The hydrogen chloride formed in the combustion chamber is cooled and absorbed in a hydrochloric acid absorption plant as described in the section on absorption systems.

Emissions

As shown in Table 4, almost no hydrogen chloride is emitted from synthesis plants. Chlorine is eliminated by combusting it with excess hydrogen. In the plants surveyed, no additional air pollution control equipment is used after the tails tower. The data in Table 4 were obtained from operating plants in response to questionnaires.

Table 4. HYDROGEN CHLORIDE EMISSIONS FROM SYNTHESIS PLANTS

Plant number	Plant capacity,[a] tons per day	Acid concentration, ° Bé	Exit gas conditions		Percent HCl	Pounds HCl emitted per ton of 20° Bé acid produced
			Volume, cfm	Temperature, ° F		
S-1	33	20	85	NA	<0.01	<0.035
S-2	100	22	NA	70	0	None
S-3	32.5	20	130	80	Trace	Trace

[a]20° Bé (31.5 percent) HCl.

NA = not available.

During startup and shutdown the possibility exists that chlorine and hydrogen chloride may be released into the air. Normally, an inert purge system is a part of the control system and any chlorine, hydrogen, or hydrogen chloride present in the system is purged through the absorber-cooler and tails tower before a shutdown.

In the event of an emergency shutdown of a hydrochloric acid plant, the hydrogen chloride gas source should be shut down first. Liquid flow to absorption equipment should be maintained at a level sufficient to keep all tubes and/or packing wetted and thus prevent hydrogen chloride emissions to the atmosphere. Some weak acid will be made during this shutdown period, but this can usually be adjusted by producing material of somewhat higher-than-normal strength later. This technique of maintaining at all times the flow of more liquid than is required for surface wetting should also be used to prevent hydrogen chloride emissions during routine shutdowns and startups.

Control of Emissions

The design, operation, and maintenance of synthesis plants result in no significant emissions of hydrogen chloride, as shown in Table 4.

MANNHEIM PROCESS

Introduction

The Mannheim process is the principal process used to produce hydrochloric acid from salt and sulfuric acid. It also produces salt cake, Na_2SO_4, which is used in glass and paper manufacturing. The chemical reactions for the salt and sulfuric acid process are:

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

$$NaCl + NaHSO_4 \longrightarrow Na_2SO_4 + HCl$$

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$$

Salt and an excess of sulfuric acid are fed into the top center of a Mannheim furnace, as shown in Figure 5, where the mixture is heated to about 1,000° F. This feed is constantly mixed and moved toward the outside of the furnace by plows until it is discharged through an opening into a pan or conveyor.

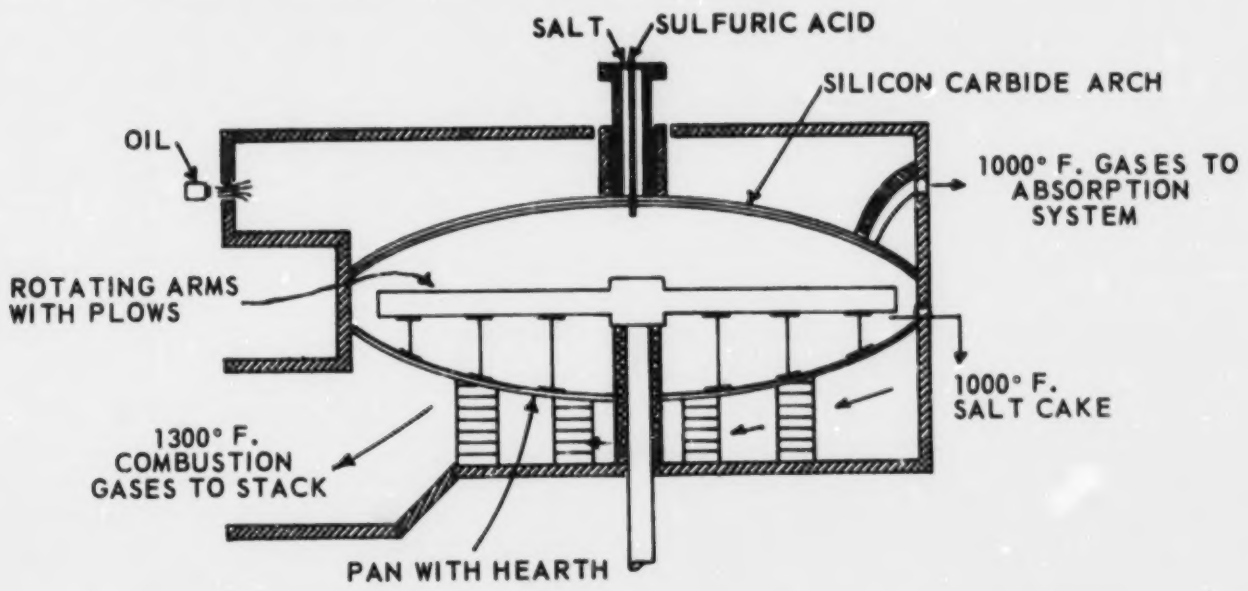


Figure 5. Cross-sectional view of Mannheim furnace.

Hot gases containing 30 to 60 percent hydrogen chloride in air go to the falling film absorber where the hydrogen chloride is cooled and absorbed.

Gases from the furnace contain sulfuric acid vapor that condenses to a mist when the gases are cooled. This mist is partially absorbed together with the hydrogen chloride and becomes an impurity in the hydrochloric acid.

Although the several types of Mannheim furnaces in use differ somewhat in detail, they all consist essentially of stationary circular muffles made up of a pan and a domed cover (Figure 6). Size of the pans ranges from 11 to 18 feet in diameter, and construction is of cast iron or refractory. The dome is cast iron or silicon carbide. Agitation of the reaction mass is accomplished by rotating arms that have plows mounted on a centrally located under-driven shaft. A firebrick enclosure provides insulation and directs combustion gases over the cover. Mannheim furnaces generally have salt cake capacities ranging from 6 to 24 tons per day.

A gas duct, a cyclone, and a gas cooler are usually considered a part of the furnace installation. The gas ducting allows the gases to cool somewhat before entering the cyclone. The cyclone removes the salt cake that is carried out with the gases, and the cooler cools the gases before absorption. A careful choice of construction materials is required. Heat resistance is of primary concern ahead of the cooler, and corrosion resistance is of importance downstream of the cooler where sulfuric and hydrochloric acids have condensed.

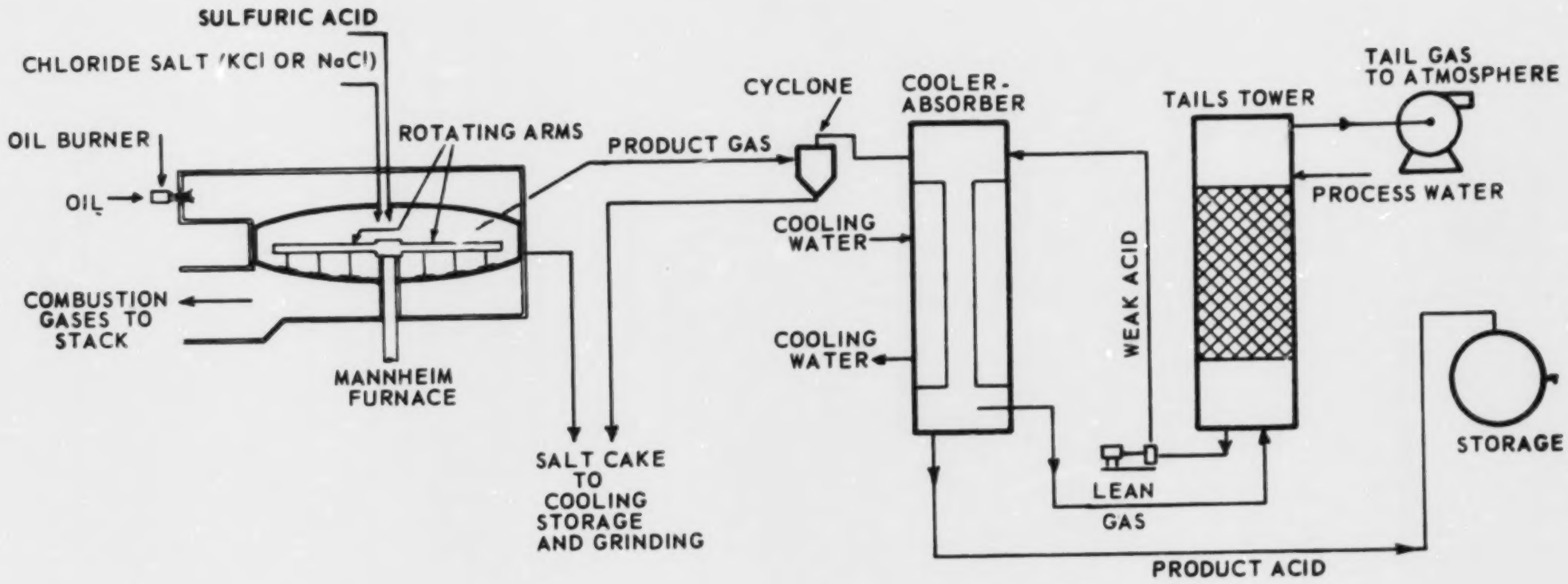


Figure 6. Mannheim hydrochloric acid manufacturing process flow diagram.

Emissions

In addition to hydrogen chloride gas, both sulfuric and hydrochloric acid mists are emitted from Mannheim process plants. Data in Table 5 show that in general, emissions from such plants are higher than those from by-product or synthesis process plants. Data reported by manufacturers and collected by actual test showed hydrogen chloride emissions of 1.3 to 3.8 pounds per ton of acid produced. These emissions are probably higher because of poor operation and maintenance and in some cases poor design of absorption systems.

Particulate emissions also occur from the salt cake as it is discharged, pulverized, and handled.

During startup and shutdown, emissions will not occur when the exhaust fan is on, and the hydrogen chloride gas and fumes are sucked through the furnace to the absorber. Liquid flow in the absorber must be maintained.

Control of Emissions

Three basic methods of controlling atmospheric emissions exist. They are proper operation, an efficient emissions collecting system, and effective maintenance. Proper operation assumes good design, and results in maximum product recovery, thus reducing the possibility of hydrogen chloride emissions. An adiabatic wet-scrubbing tower that utilizes hydrochloric acid has been used with good results both to scrub and to cool the furnace gas.

To reduce atmospheric emissions, a scrubber system can be installed on the tails tower exhaust. Scrubbers presently in use for this purpose include venturi scrubbers and packed water scrubbing towers.

The few remaining Mannheim plants in this country are gradually being retired from service because of their high cost of operation and maintenance.

HARGREAVES PROCESS

Introduction

The Hargreaves process was developed in England, and after about 1850 it appeared as if it might become an important source of hydrochloric acid and salt cake. However, new processes were introduced and its use declined. Only one plant of this type is in operation in the United States.

In this process, hydrochloric acid is formed by the reaction of sulfur dioxide, steam (water), air (oxygen), and salt at temperatures of about 800° to 1,000° F. The formulas for the reaction are:

$$S + O_2 \longrightarrow SO_2$$

$$2\,SO_2 + 4\,NaCl + 2\,H_2O + O_2 \longrightarrow 2\,Na_2SO_4 + 4\,HCl$$

The reaction is exothermic and will maintain itself once the reactants are heated to the proper starting temperature.

Emissions

The potential emissions from the Hargreaves process are unreacted sulfur dioxide, hydrogen chloride, and salt dust. Dusts are removed initially by

Table 5. EMISSIONS FROM MANNHEIM PLANTS

Plant number	Plant capacity,[a] tons per day	Acid concentration, ° Bé	Exit gas conditions		Percent HCl	Control equipment	Substances other Than HCl present in exit gas	Pounds HCl emitted per ton of 20° Bé acid produced
			Volume, cfm	Temperature, ° F				
M-1	79	20	440	150	0.46	None	H_2SO_4, 30 ppm	3.0
M-2[b]	10	20	168	95	0.16; 0.18 0.06; 0.14	Water scrubber	H_2SO_4 and SO_2 0-160 ppm	Gas 3.5, 3.9 1.3, 3.1 Mist 0.04-0.065

[a] 20° Bé (31.5%) HCl.

[b] Tested by MCA-PHS.

cleaning the product gas with a cyclone. During periods of operational upsets or additions of new salt, hydrogen chloride or sulfur dioxide can be emitted to the air. Since the reaction occurs at 1,000° F, it is desirable to interrupt the process as little as possible, thereby preventing loss of heat and excessive emissions.

LAURY PROCESS

Introduction

In the Laury process, hydrochloric acid is produced in a rotary furnace from the reaction of sodium chloride and sulfuric acid.

The equations are:

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

$$NaCl + NaHSO_4 \longrightarrow Na_2SO_4 + HCl$$

A Laury furnace consists of an oil-fired combustion chamber that discharges into a horizontal revolving drum containing a roasting section and a grinding section (See Figure 7). Materials are charged at the end opposite the heating source. As they move counter-current to the flow of hot gases, they are mixed, ground, and roasted. The flue gases and hydrogen chloride from the roasting processes are exhausted at the same end of the drum in which the sodium chloride and sulfuric acid are charged. The hydrogen chloride gas and flue gas from the furnace are exhausted first through either a settling chamber or a cyclone to collect the dust, and then are sent to the hydrochloric acid absorber section of the plant.

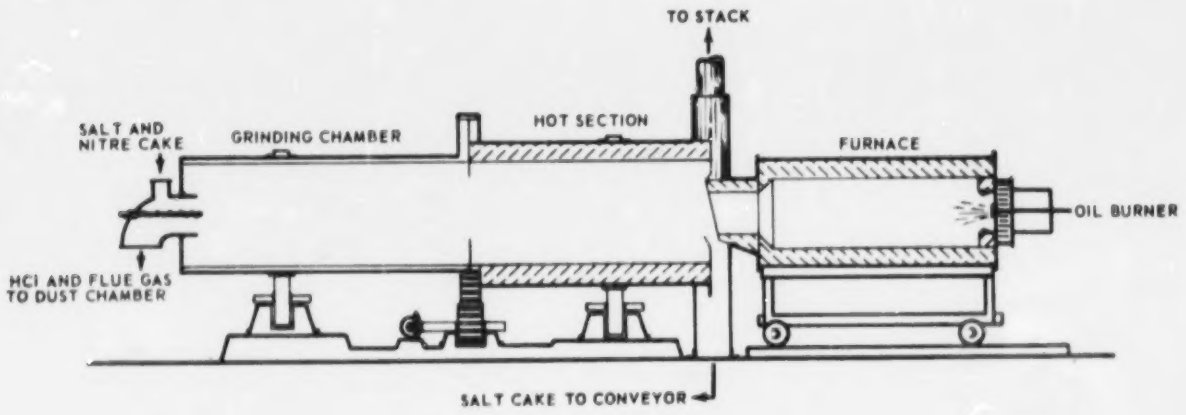


Figure 7. Cross-sectional view of Laury furnace.

This process was used before the introduction of the falling film absorber and probably all units were installed with two packed columns to absorb the hydrogen chloride.

No plants of this type currently operate in the United States.

Emissions

Emissions of hydrogen chloride from this process are low in concentration but high in volume. Other emissions from this process include salt cake dust

and sulfuric acid mist. Salt cake dust is eliminated by a dust removal system or is removed in the acid absorption system.

ANHYDROUS HYDROGEN CHLORIDE

INTRODUCTION

Anhydrous hydrogen chloride is sometimes recovered without further processing from the synthesis process. It is also produced from aqueous acid in three basic steps:

1. Thermal stripping of a strong hydrochloric acid feed to the 21 percent azeotropic mixture.
2. Cooling, condensing, and recycling part of the hydrogen chloride as reflux.
3. Cooling and removing the moisture from the gas.

Strong hydrochloric acid from storage is stripped in an impervious carbon or graphite shell-and-tube stripper or a similarly packed stripping column (Figure 8). A reboiler is required at the base of the stripper to provide thermal energy for the liquid-gas separation. Spent acid leaves the bottom of the stripper. This acid is either cooled and stored or sent to the concentration unit for cooling and concentration in a falling film absorber.

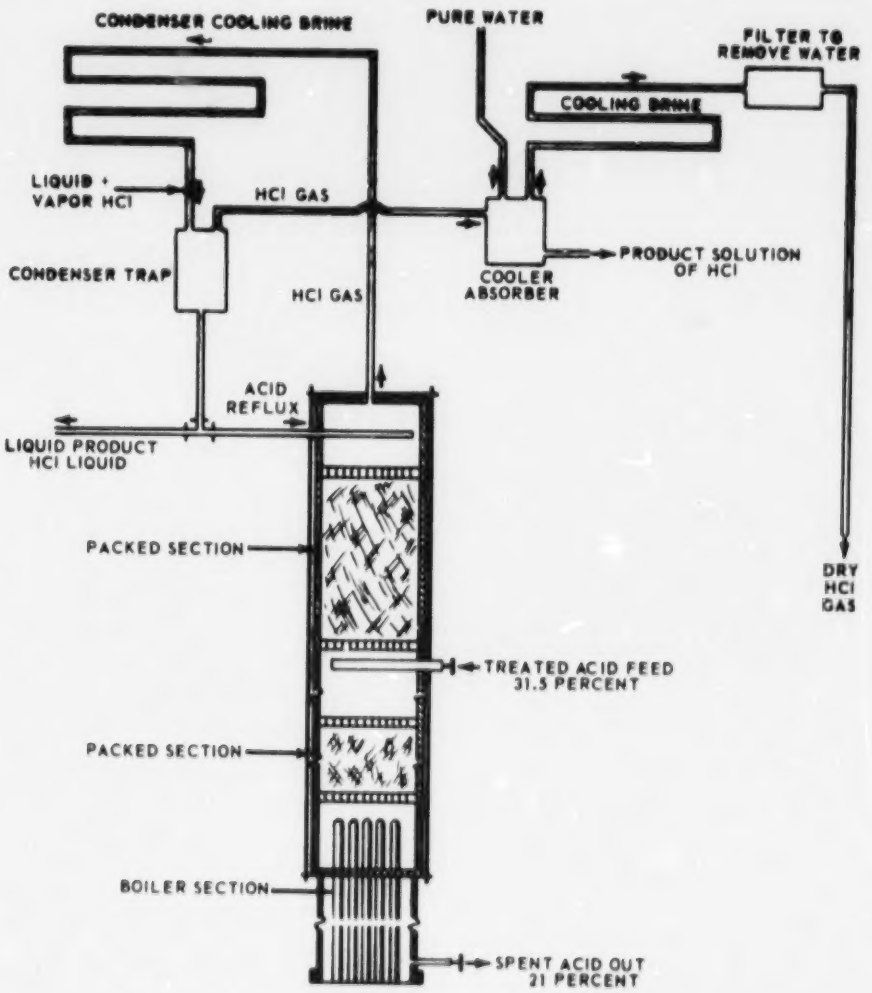


Figure 8. Hydrogen chloride distillation system for reagent-quality acids.

The hydrogen chloride gas and other vapors from the top of the stripper are passed through a heat exchanger where the condensate is removed and fed back as a reflux to the stripper. The remaining gas, which is substantially pure hydrogen chloride, is then dried in a shell-and-tube condenser with a 0° to 5° F cooling brine and then passed through a particulate entrainment separator for water removal.

A complete unit that will produce anhydrous acid is available from several hydrochloric acid equipment manufacturing companies. These units operate in a similar fashion to the process described here.

EMISSIONS

This process yields no emissions to the atmosphere because the manufacturing system is closed and the product vapors are piped directly to the process area.

REAGENT-GRADE HYDROCHLORIC ACID MANUFACTURE

Commercial-grade 31.5 percent hydrochloric acid is distilled in a rectifying column to form reagent-grade 37 to 38 percent hydrochloric acid. Packaged commercial systems for making reagent acid, as illustrated in Figure 8, are available.

A system for making the reagent-grade acid may also make dry hydrogen chloride gas and hydrochloric acid solutions. These systems are made up of a boiler at the base of a split column, a feed to the column (at the split section) that serves as reflux for the acid being vaporized, a condenser that forms product hydrogen chloride and refluxes the hydrogen chloride gas section of the column, and a cooler-absorber for forming 31.5 percent hydrochloric acid product if desired. The system is valved so that any one of the three desired products can be made with only a change of valving. A flow diagram of a plant of the type described is illustrated in Figure 8.

Other types of plants making reagent-grade acid are not of the "package" type. These plants are constructed largely of glass and have tantalum or titanium heat exchangers for condensing the acid.

Any acid must be treated before it is distilled. Minerals and gases, which may carry over with the acid vapors, must be stabilized to stay in the 21 percent azeotropic acid remaining after boiling. Processes for stabilizing the minerals and gases are proprietary and differ with the acid manufacturer. The azeotropic mixture of acid remaining after distillation can be used to absorb more hydrogen chloride and then be redistilled, or it can be used in other processes.

Reagent-grade acid may also be made directly from a relatively pure gas such as is produced in the synthesis process without the need for chemical treatment or distillation.

EMISSIONS

This process yields no emissions to the atmosphere because the manufacturing system is closed.

AIR BLOWING

Air blowing, used to remove organic substances from hydrochloric acid, can cause hydrogen chloride and organic emissions that can be a potential source of odors. Fortunately, this obsolete practice is seldom used and is of little industrial importance.

In the process, air is blown through a sparger installed in a tank of hydrochloric acid to remove dissolved organic gases and to evaporate organic materials in the acid. This blowing may take place for a 30- to 60-minute period.

Emissions from air blowing can be eliminated by water scrubbing the gases

vented from the tank. A water ejector can be used to remove the fumes from the tank as well as to scrub them.

No reports of air blowing practices were obtained during the preparation of this report.

HYDROGEN CHLORIDE ABSORPTION SYSTEMS

Falling Film Absorber

The most widely used absorption unit is the falling film system. It consists of a falling film cooler-absorber and a small packed tails tower.[5,6] As shown in Figures 9 and 10, the gases and the absorbent, which is usually weak acid, enter at the top of the absorber and the hydrogen chloride is absorbed in the liquid wetting the inside of the tube. The absorption is limited by the number of tubes, which determines the amount of wetted area available for absorption and cooling.

After passing through the falling film absorber, the gases pass through a tails tower where the remaining portion of the hydrogen chloride is reduced to less than 0.5 percent of the exit gas. Fresh water, which is used as the absorbant, is fed to this tower, and a weak acid results from the absorption of the hydrogen chloride in the water.

Adiabatic Absorber

Another system that is relatively new is the adiabatic absorption unit,[6,7] shown in Figure 11. Used to make an organic-free acid, this unit consists of a packed column into which water is fed near the top, and hydrogen chloride near the bottom. Hydrogen chloride and water contact one another to form hydrochloric acid that is at its boiling point. Excess heat is removed by the formation of steam. Inert substances, steam, and lower-boiling organic materials that cannot condense in the acid because it is at its boiling point are vented from the column. A water ejector-type scrubber is usually used to scrub the gases coming from the column.

Further removal of organic materials may be accomplished by cooling the acid and running it through a carbon bed where the organics are absorbed.

A variation of this plant is the modified adiabatic absorption unit. It is not a true adiabatic system in the usual sense; it is designed to remove more organic substances and chlorine. In this process, hydrogen chloride gas is injected near the middle of the column to maintain an adiabatic section in the upper portion of the column. Heat then can be added to the bottom of the column to strip the acid in the bottom section of the column. These plants are usually sold complete with instruments.

Emissions from Absorber Systems

Hydrogen chloride emissions from a falling film absorber may be influenced by several factors.[8] These include a lack of cooling and a lack of sufficient weak acid to absorb the hydrogen chloride gas. During startups and shutdowns when hydrogen chloride gas flow is less than normal, it is possible that not all of the tubes in the absorber will be wetted if the feed water rate is reduced to maintain product strength. In this situation gas passes through the falling film

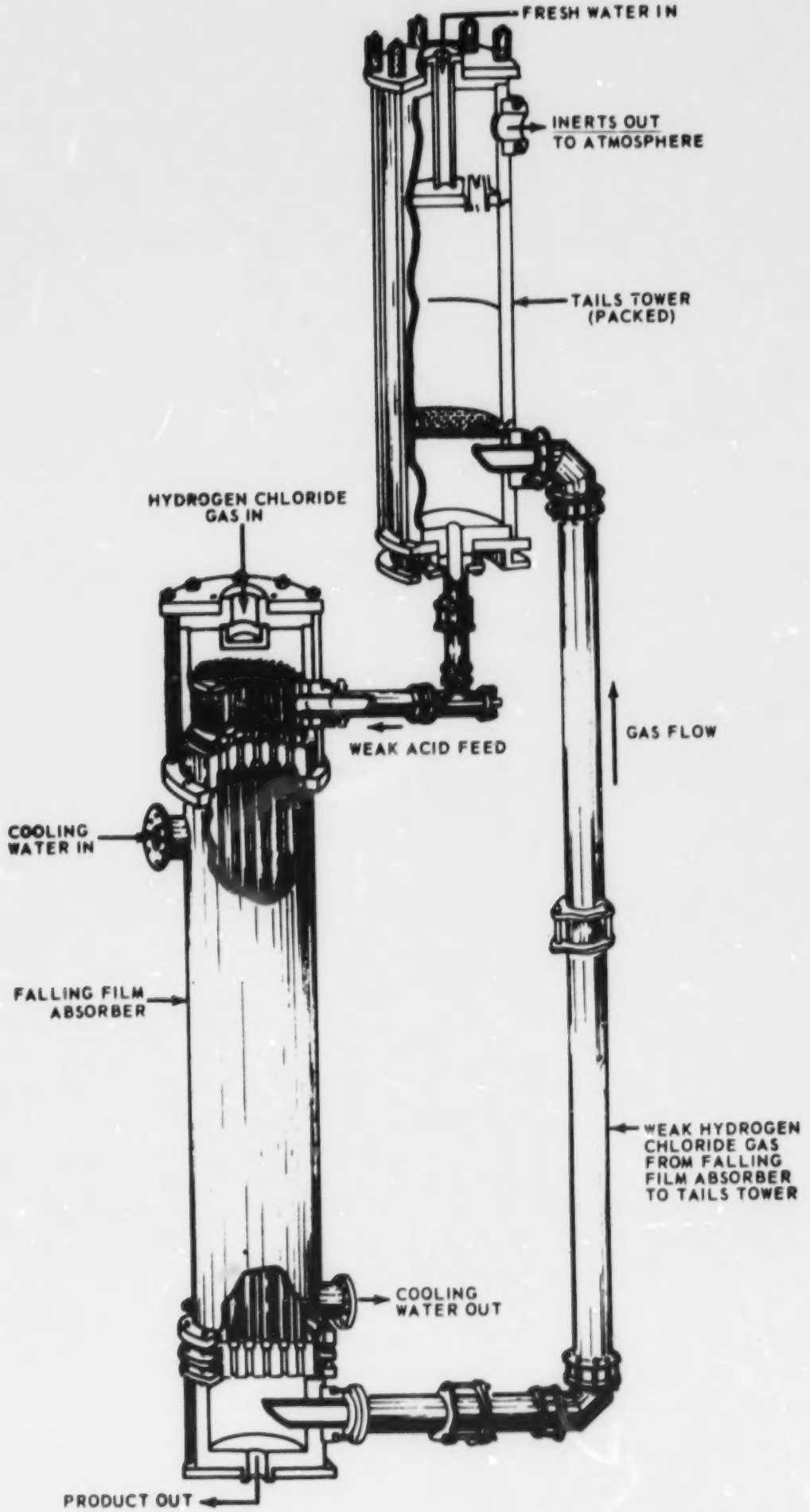


Figure 9. Falling film absorber with external piping and tails tower.

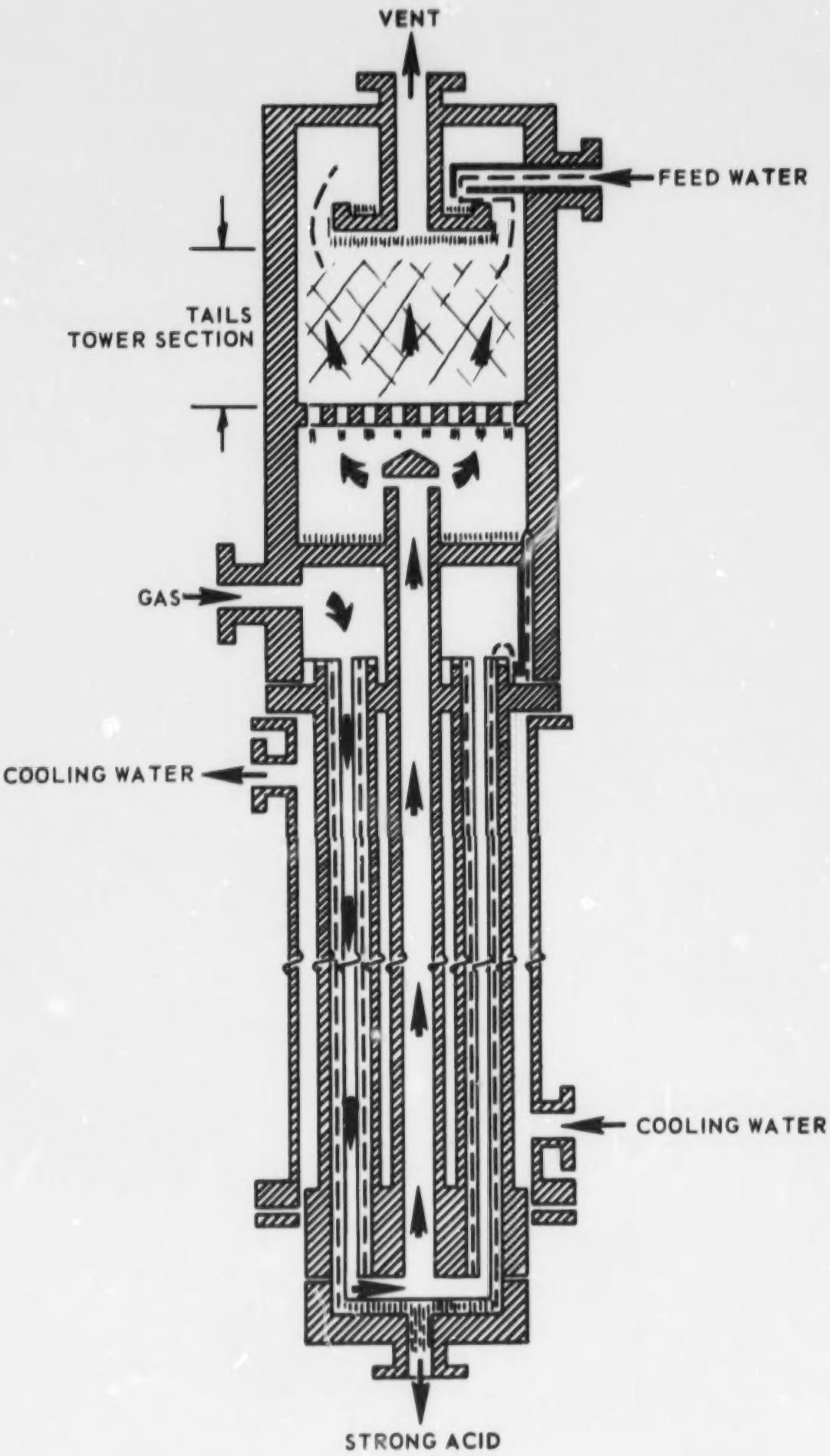
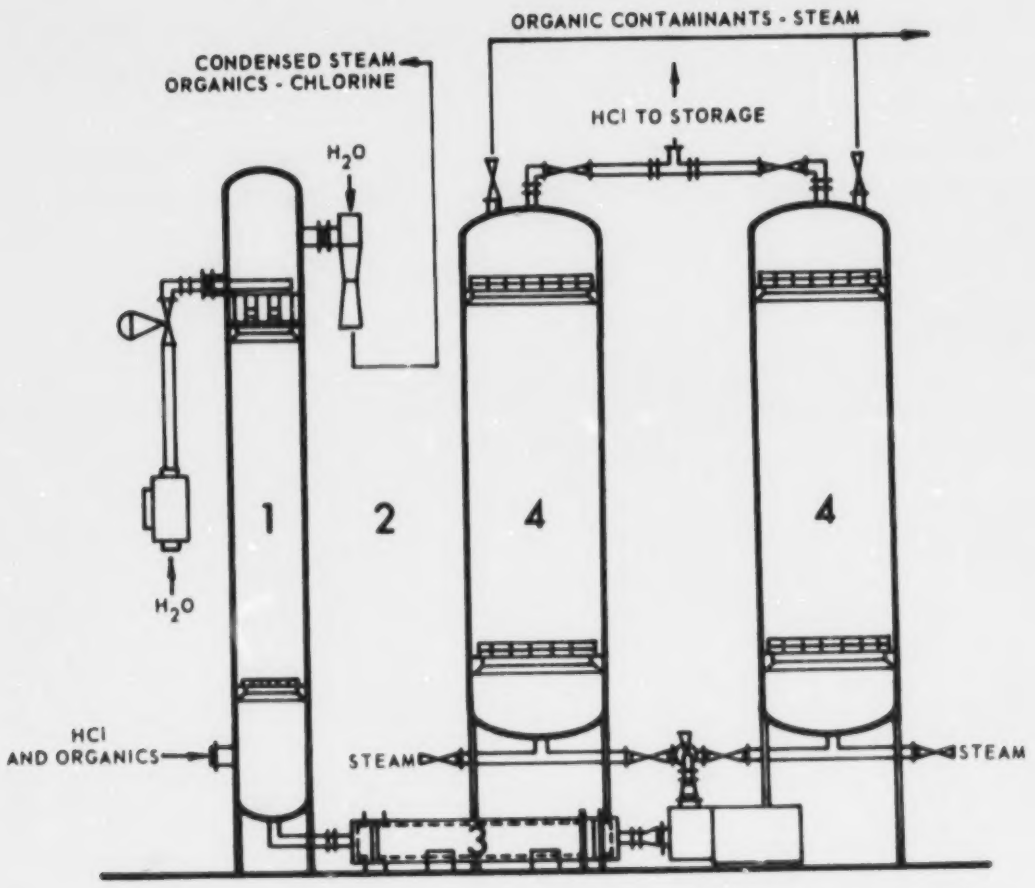


Figure 10. Falling film absorber with integral gas piping and tails tower.



1. ADIABATIC ABSORPTION TOWER RECEIVES BY-PRODUCT HCl GAS STREAM CONTAMINATED WITH ORGANICS. ABSORPTION OF HCl IN WATER GENERATES HEAT.
2. TOWER OVERHEAD CONDENSES BY DIRECT CONTACT FUME SCRUBBER.
3. HOT HCl SOLUTION COOLED BY SHELL AND TUBE COOLER.
4. COOLED HCl SOLUTION PUMPED TO EITHER OF TWO ACTIVATED CARBON ADSORBERS ACTING ON ADSORB-REGENERATE CYCLE. ORGANIC CONTAMINANTS ADSORBED IN CARBON RESULTING IN FINISHED ACID. 32% CONCENTRATION CONTAINING LESS THAN 1 ppm ORGANICS AT 100°F. ACID NOW TRANSFERRED TO STORAGE AREA.

Figure 11. Typical adiabatic hydrochloric acid absorption unit flow diagram.

unit and overloads the tails tower, which also is receiving less than a normal amount of feed water.

The solution to this problem is to maintain a minimum flow sufficient to wet the tubes. Weak acid produced during these periods can either be discarded or concentrated by making higher-strength acid when normal conditions are restored.

The adiabatic absorption unit is not nearly as sensitive to cooling problems as the falling film unit because heat is removed by the formation of steam. It is, however, just as likely to produce hydrogen chloride emissions if all of the packing is not wetted. The technique of maintaining minimum liquid flow as described above is also effective with the adiabatic unit. The adiabatic unit, with its counter flow liquid and gas, is more easily flooded than the parallel-flow falling film unit.

Control of Emissions

Hydrogen chloride emissions may be effectively controlled by installing any of several types of scrubbers after the tails tower in the case of the falling film unit and after the adiabatic tower in the case of the adiabatic unit. Regardless

of the type of absorption unit used for making hydrochloric acid, the best design is characterized by a final scrubber to remove residual hydrogen chloride passing through the system.

An adiabatic absorption system normally has a scrubber designed to reduce the hydrogen chloride content of the gases emitted to 0.5 percent or less by volume.

DEFINITIONS

Absorber	Chemical equipment that serves to contact a gas or vapor with a liquid so that gas or vapor is absorbed into the liquid. In this report, it refers to equipment used to contact hydrogen chloride with water to form hydrochloric acid.
Absorption system	An absorber or several absorbers used to absorb hydrogen chloride.
Acid mist	Extremely small particles of liquid acid that are suspended in a gas or vapor.
Baumé (Bé)	Acid strength is determined by use of a floating instrument (hydrometer) calibrated to read degrees Baumé and by a conversion chart. The Baumé can also be calculated if the specific gravity of the acid is known: $^{\circ}\text{Bé} = 145 - \left(\frac{145}{\text{sp gr}}\right)$
Contaminant	Any substance not normally found in the atmosphere.
Emission	Any gas or vapor stream emitted to the atmosphere.
Establishment	A works having one or more hydrochloric acid plants or units, each of which is a complete production entity.
Muriatic acid	20° Bé hydrochloric acid.
Plant	A chemical works at which hydrogen chloride is manufactured and converted with an absorption unit into hydrochloric acid.
Reforming	Burning an organic fuel in the presence of water or water vapor in such a manner that hydrogen-rich gas is formed.
Tail gas	Gases and vapors that leave hydrochloric acid absorption units.

APPENDICES

A. SAMPLING AND ANALYTICAL TECHNIQUES

B. HYDROCHLORIC ACID MANUFACTURING ESTABLISHMENTS LOCATED IN UNITED STATES

C. PHYSICAL DATA–HYDROCHLORIC ACID

APPENDIX A. SAMPLING AND ANALYTICAL TECHNIQUES

DETERMINATION OF HYDROGEN CHLORIDE AND CHLORINE IN STACK GAS.

The method discussed herein is used to determine the presence of hydrogen chloride in the stack gases from hydrochloric acid manufacturing processes. Samples are collected from the gas stream in either midget impingers or a grab-sampling bottle containing sodium hydroxide, and hydrogen chloride is determined by the Volhard titration.[9] If chlorine is suspected to be present in the stack emission, another sample is collected in a similar manner, except that a known quantity of alkaline arsenite absorbing reagent is substituted for sodium hydroxide. Chlorine is reduced to chloride by arsenite, and is measured by titration of the unconsumed arsenite with standard iodine solution. Total chloride content of the sample is determined by the Volhard titration. Hydrogen chloride concentration is calculated by subtraction of the chlorine concentration from total chloride concentration. This method is applicable in determining hydrogen chloride and chlorine concentrations ranging from 10 ppm to percentage quantities.

Reagents

All chemicals must be ACS analytical reagent-grade.

Water

Deionized or distilled water.

Absorbing Reagents:

1. Sodium hydroxide (1 N) – Dissolve 40 g of sodium hydroxide in water and dilute to 1 liter. This reagent is used when the stack gas concentration of hydrogen chloride is suspected to be less than 1,000 ppm.
2. Sodium hydroxide (2.5 N) – Dissolve 100 g of sodium hydroxide in water and dilute to 1 liter. This reagent is used when the stack gas concentration of hydrogen chloride is suspected to be greater than 1,000 ppm.
3. Alkaline arsenite (1 N NaOH and 0.1 N $NaAsO_2$) Dissolve 40 g of NaOH and 6.5 g of sodium arsenite ($NaAsO_2$) in water and dilute to 1 liter in a volumetric flask. This reagent is used when the stack gas concentration of hydrogen chloride and Cl_2 is suspected to be less than 1,000 ppm.
4. Alkaline arsenite (2.5 N NaOH and 0.5 N $NaAsO_2$) Dissolve 100 g of NaOH and 32.5 g of $NaAsO_2$ in water and dilute to 1 liter in a volumetric flask. This reagent is used when the stack gas concentration of hydrogen chloride and Cl_2 is suspected to be greater than 1,000 ppm.

Ferric Alum Indicator

Dissolve 28.0 g of ferric ammonium sulfate $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 70 ml of hot water. Cool, filter, add 10 ml of concentrated nitric acid (HNO_3), and dilute to 100 ml in a volumetric flask.

Nitric Acid (8N)

Prepare NO_X-free nitric acid by adding 100 ml of HNO_3 to 100 ml of water and boiling in a flask until the solution is colorless. Store in a glass reagent bottle.

Nitrobenzene

Reagent grade.

Sodium Chloride (Primary Standards)

1. NaCl (0.1 N) – Dissolve 5.846 g of dried sodium chloride (NaCl) in water and dilute to 1 liter in a volumetric flask.
2. NaCl (0.01 N) – Dissolve 0.5846 g of dried NaCl in water and dilute to 1 liter in a volumetric flask, or dilute 100 ml of 0.1 N NaCl to 1 liter.

Ammonium Thiocyanate

1. NH_4CNS (0.1 N) – Dissolve 8 g of NH_4CNS in water and dilute to 1 liter in a volumetric flask.
2. NH_4CNS (0.01 N) – Dilute 100 ml of 0.1 N NH_4CNS to 1 liter in a volumetric flask, or dissolve 0.8 g NH_4CNS in 1 liter of distilled water.

Silver Nitrate

1. $AgNO_3$ (0.1 N) – Dissolve 17.0 g of silver nitrate ($AgNO_3$) in water and dilute to 1 liter in a volumetric flask. Transfer to an amber reagent bottle. Standardize this solution against 0.1 N NaCl solution, according to the Volhard titration.[9]
2. $AgNO_3$ (0.01 N) – Dissolve 1.7 g of $AgNO_3$ in water and dilute to 1 liter in a volumetric flask. Transfer to an amber reagent bottle. Standardize this solution against standard 0.01 N NaCl solution, according to the Volhard titration.

Starch Solution (Iodine Indicator), 1.0%

Make a thin paste of 1 g of soluble starch in cold water and pour into 100 ml of boiling water while stirring. Boil for a few minutes. Store in a glass-stoppered bottle.

Standard Iodine Solution (0.1 N)

Dissolve 12.69 g of resublimed iodine (I_2) in 25 ml of a solution containing 15 g of iodate-free potassium iodine (KI); dilute to 1 liter in a volumetric flask. Standardize this solution against a standard thiosulfate solution using starch as an indicator. This solution should be stored in an amber reagent bottle and refrigerated when not in use.

Apparatus

(See Figures A-1 and A-2)

Sampling Probe

10-mm Pyrex® glass tubing of any convenient length.

Filter

A small fiberglass filter may be fitted to the probe inlet when particulate matter is present in the gas stream being sampled.

Heating Tape

Used to heat probe.

Variable Voltage Regulator

Used to regulate probe heating.

Dry Gas Meter

Readable to the nearest 0.01 cubic foot.

Vacuum Pump

A diaphragm-type pump rated at 15 liters per minute.

Absorbers

1. Midget impinger — An all-glass midget impinger sampling train capable of removing hydrogen chloride and chlorine from a gas sample may be used when sampling stack gas suspected of containing less than 0.1 percent hydrogen chloride or chlorine.

   The sampling train should consist of a probe, four midget impingers, a gas drying tube, a vacuum pump, and a flow meter, as illustrated in Figure A-1.

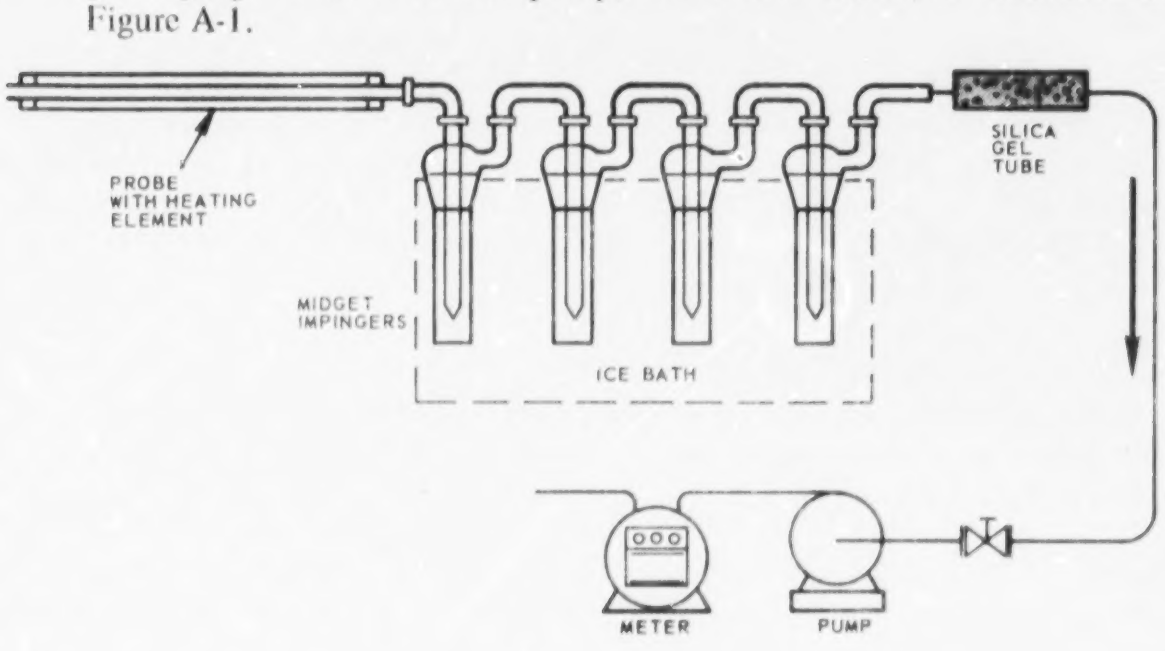


Figure A-1. Impinger gas sampling train.

A Pyrex® glass tube serves as the probe. It should have a ball joint on the outlet to which other glassware can be easily connected. The probe should be wrapped with nickel-chromium heating wire, insulated with glass wool and installed into a protective 1-inch-diameter stainless steel

tube. During sampling, the heating wire is connected to a calibrated, variable transformer to maintain a temperature of up to 250° F on the probe wall. A heating tape may also be used to heat the probe.

Four midget glass impingers are connected in series to the probe outlet with glass ball joints. The first three impingers each contain 15 ml of absorbing reagent. The fourth impinger is left dry to catch any material that is carried over from the other impingers. All four impingers are cooled in an icewater bath.

Gases leaving the impingers are dried as they pass through a tube of silica gel. They then are pumped to the airtight vacuum pump and gas meter. Sampling rates are regulated by using a valve to adjust the flow through the pump.

2. Grab-sampling bottle An accurately calibrated 2-liter glass bottle equipped with Teflon® stopcocks (Figure A-2) should be used when sampling percentage quantities of hydrogen chloride or chlorine. Absorbing reagent is added to the grab-sample bottle after the sample has been collected.

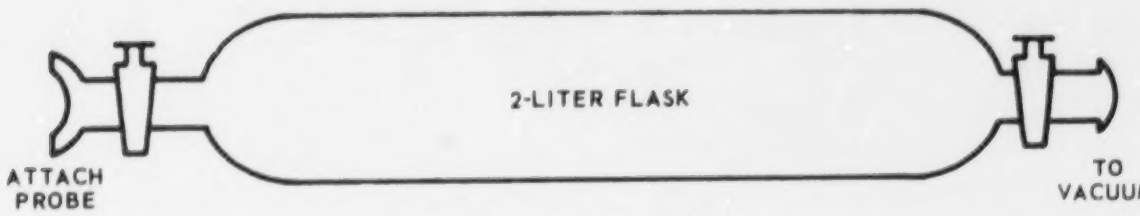


Figure A-2. Grab sample bottle.

Dispenser (Absorbing Reagent)

A 100-milliliter round-bottom flask, modified with a Teflon® stopcock and ball joint extension (see Figure A-3) is used as a dispenser for absorbing reagent. It is used to add reagent to the grab-sampling bottle after the sample has been collected.

Analytical Procedure

Collection of Samples

1. Midget impinger train:
   Pipet 15 ml of absorbing reagent into each of the three midget impingers. Heat probe to prevent moisture condensation. Start pump and sample at a rate of 1 to 3 liters per minute for at least 60 minutes.
2. Grab sampling:
   Flush probe and draw about 20 liters of gas through the sample bottle. Pipet 25 ml of absorbing reagent into the dispenser and add to the grab-sample bottle following collection of the sample. Shake bottle thoroughly for about 2 minutes to insure complete absorption.
3. Transfer the contents of the impingers or grab-sampling bottle to a sample container, such as a polyethylene bottle, containing deionized or distilled water.

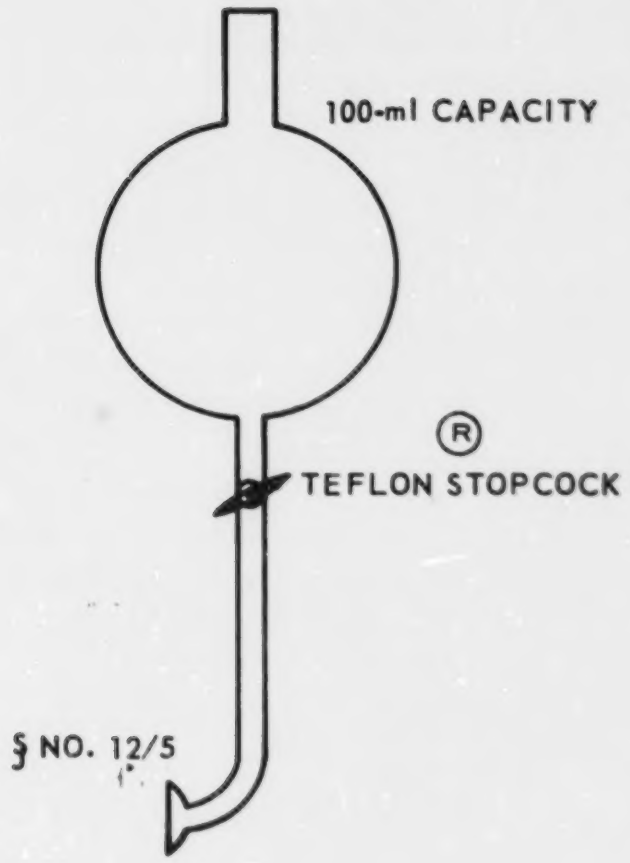


Figure A-3. Burette for adding absorbing reagent.

Sample Preparation

Measure the actual volume of the liquid sample or adjust to a known volume using a graduated cylinder or volumetric flask.

Procedure A

Analysis of Hydrogen Chloride

Pipet an aliquot of the sample into a 250-ml Erlenmeyer flask. Add 25 ml of water, 5 ml of nitric acid and swirl to mix. Depending on chloride content, add 0.1 N or 0.01 N silver nitrate from a buret until the silver chloride formed begins to coagulate. When coagulation occurs, add an additional 5 ml of silver nitrate. Add 3 ml of nitrobenzene and 2 ml of ferric indicator, then back-titrate with 0.1 N or 0.01 N ammonium thiocyanate until the first appearance of the reddish-brown $Fe(CNS)_6^{-3}$ complex. A blank determination for chloride in the absorbing reagent should be run simultaneously and subtracted from the sample results. From the titer of NH_4CNS solution, as determined previously by titration against standard $AgNO_3$ solution using ferric alum as an indicator, calculate the net volume of $AgNO_3$ required for precipitation of the chloride.

Calculations

Compute the number of milligrams of hydrogen chloride present in the sample by the following equation:

$$C = HCl, mg = \text{net ml } AgNO_3 \times T \times F$$

T = hydrogen chloride equivalent of standard $AgNO_3$

(T = 3.65 mg HCl/ml for 0.1 N $AgNO_3$)

(T = 0.365 mg HCl/ml for 0.01 N $AgNO_3$)

$$F = \frac{\text{sample volume, ml}}{\text{aliquot volume, ml}}$$

Convert the volume of gas sampled to the volume at standard conditions of 70° F and 29.92 in. Hg.

$$V_s = V \times \frac{P}{29.92} \times \frac{530^\circ R}{(t + 460^\circ R)}$$

V = volume of gas sampled, as measured on dry gas meter or equal to volume of grab sample bottle—liters
P = barometric pressure (in. Hg) or absolute pressure at gas meter
t = average temperature of gas sampled, ° R

Determine the concentration of hydrogen chloride in the gas sample by the following formula:

$$\text{ppm HCl} = \frac{(662)\ (C)}{V_s}$$

662 = µl/mg of HCl at 70° F and 29.92 in. Hg
C = concentration of HCl, mg
V_s = volume of gas sampled in liters at 70° F and 29.92 in. Hg

Procedure B

Analysis of Hydrogen Chloride in the Presence of Chlorine

Pipet an aliquot of the sample into a 250-ml Erlenmeyer flask and proceed with the Volhard titration for total chlorides as described under Procedure A. A blank determination for chloride in the absorbing reagent (alkaline-arsenite reagent) should be run simultaneously and subtracted from the sample results.

Pipet another aliquot of the sample into a 250-ml Erlenmeyer flask. Add a few drops of phenolphthalein indicator, neutralize carefully with concentrated hydrochloric acid, and cool. Add sufficient solid sodium bicarbonate ($NaHCO_3$) to neutralize any excess hydrochloric acid, then add 2 to 3 g more. Add 2 ml of starch indicator and titrate with 0.1 N iodine solution to the blue endpoint. For the reagent blank, determine the number of ml of 0.1 N I_2 required to titrate 25 ml of alkaline-arsenite absorbing reagent, as described above.

Calculations

Determine the number of milliliters of 0.1 N I_2 required to titrate the entire sample by the following formula:

$$\text{Sample (ml 0.1 N } I_2\text{)} = \text{(ml of 0.1 N } I_2 \text{ for aliquot)} \times F$$

$$F = \frac{\text{volume of sample, ml}}{\text{volume of aliquot, ml}}$$

$$Cl_2, \text{mg} = \text{Blank (ml 0.1 N } I_2\text{)} - \text{Sample (ml 0.1 N } I_2\text{)} \times 3.546$$

3.546 = chlorine equivalent of 0.1 N I_2, mg

Convert the volume of gas sampled at standard conditions of 70° F, 29.92 in. Hg, using the formula in Procedure A. Calculate the concentration of Cl_2 in the sample using the following formula:

$$\text{ppm } Cl_2 \text{ by volume} = \frac{(340)(C)}{V_s}$$

340 = 1/mg of Cl_2 at 70° F and 29.92 in. Hg

C = concentration of Cl_2, mg
V_s = volume of gas sampled at standard conditions, liters

Determine the number of milligrams of hydrogen chloride present in the sample by subtracting the number of milligrams of chlorine present, as determined by the iodine titration, from the total number of milligrams of chloride present as determined by the Volhard titration. Calculate the concentration of hydrogen chloride in parts per million using the formula in Procedure A.

Total stack gas volume must also be measured in order to determine the emissions on a weight basis. This may be done by measuring the gas velocity with a pitot tube.

The following equations are used to determine gas velocity and gas volume:

$$V_S = 172\,(F)\,(\sqrt{\Delta P \text{ avg}})\left[\sqrt{T_S} \times \frac{29.92}{P_S} \times \frac{29.0}{M_S}\right]$$

V_S = velocity in feet per minute at stack conditions
F = pitot tube correction factor (0.85 for type S)
M_S = molecular weight of stack gas
T_S = average stack gas temperature ° R
P_S = average stack gas pressure, in. Hg
ΔP = pitot tube manometer reading, in. water

The total stack gas volume is then:

$$Q_s = (V_S)(A)\left[\frac{P_S}{T_S}\right] \quad (17.4)$$

A = stack area, sq ft
Q_s = gas volume, ft^3/min at 70° F and 29.92 in. Hg

The emissions on a weight per hour basis may then be determined by the following equation:

$$W = ppm \times 10^{-6} \times Q_s \times 60 \times \frac{\text{mol wt}}{387}$$

W = emissions, lb/hr
ppm = parts per million by volume of contaminant
Q_s = stack gas flow rate, scfm
mol wt = molecular weight of contaminant
Cl_2 = 70.92 HCl = 36.46
387 = volume (ft^3) occupied by 1 lb mol at 70° F and 29.92 in. Hg

Discussion of Procedure:

The estimated error for the combined sampling and analytical procedure is ±10 percent. The precision of the analytical methods is ±2 percent on standard samples containing NaCl and $NaAsO_2$.

The usual volumetric errors are encountered with the Volhard titration. Premature endpoints may occur if the NH_4CNS is not added by drops near the equivalence point and the solution shaken before the next addition. Nitrobenzene is used to effectively remove AgCl by forming an oily coating on the precipitate and preventing reaction with the thiocyanate.[10] Bivalent mercury, which forms a stable complexion with the thiocyanate, and substances that form insoluble silver salts interfere in the analysis and must be absent from the sample. Titration should be made at temperatures below 25° C, as is customary in other titrations with thiocyanate.[11]

The chief source of error in the iodine titration of arsenite is the failure to use sufficient bicarbonate to neutralize all the excess acid. If insufficient bicarbonate is added, serious errors may be incurred because of a fading endpoint. A reducing agent such as sulfur dioxide and oxidizing agents such as iodine, nitrogen dioxide, and ozone interfere with the iodine titration and yield high results when present in the stack gas sample.

ACID MIST SAMPLING.

The sampling apparatus is made up of a probe, a cyclone, a filter, four impingers, a dry gas meter, a vacuum pump, and a flow meter, as shown in Figure A-4.[12,13]

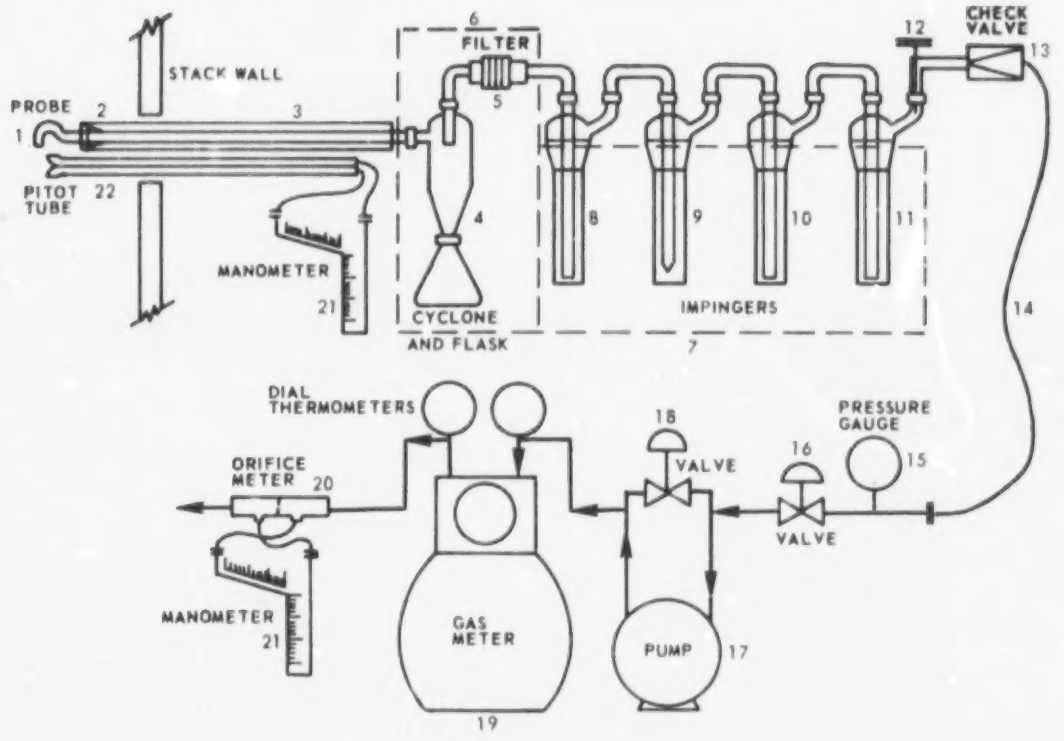


Figure A-4. Mist sampling train.

A stainless steel, buttonhook-type probe tip (1) is connected to the probe by a stainless steel coupling (2) and Viton® "O" ring bushings.

The probe (3) is a 5/8-inch-outside-diameter medium-wall Pyrex® glass tube with an S-ball joint on one end. The glass probe is wound from the entrance end with 25 feet of 26 guage nickel-chromium wire. During sampling the wire is connected to a calibrated variable transformer to maintain a gas temperature of 250° F in the probe. The wire-wound glass tube is wrapped with fiberglass tape and encased in a 1-inch-outside-diameter stainless steel tube for protection.

A glass cyclone (4) is connected to the outlet end of the probe to catch larger size mists.

A very coarse-fritted glass filter holder (5), which holds a 2-½-inch tared glass fiber filter of MSA type 1106 BH filter paper, follows the cyclone.

The cyclone and filter are contained in an electrically heated, enclosed box (6), the temperature of which is thermostatically maintained at a minimum of 250° F to prevent condensation of water.

Four impingers in series, placed in an ice bath, are connected to the filter holder outlet. The first impinger is a Greenburg-Smith design modified by replacing the tip with a ½-inch diameter glass tube extending to 0.5 inch from the bottom of the flask. This impinger contains 100 ml of sodium hydroxide. The second impinger is a Greenburg-Smith impinger with tip that also contains 100 ml of sodium hydroxide. The third impinger is modified the same as the first and is left dry. The fourth impinger (11) is also a modified Greenburg-Smith type. It contains about 175 g of dry silica gel.

From the fourth impinger (11) the effluent stream flows through a check valve (13), a needle valve, a leakless vacuum pump, and a dry gas meter. A calibrated orifice and a dual manometer complete the train and are used to measure instantaneous flow rates.

DETERMINATION OF SULFATES AND SULFURIC ACID.

This method is used to determine concentrations of sulfuric acid or sulfur dioxide[14] in stack gases from the manufacture of hydrochloric acid by the Mannheim process.

Sulfur dioxide in the stack effluent is absorbed and oxidized to the sulfate form in midget impingers containing 3 percent hydrogen peroxide.

Sulfuric acid mist is collected on a glass fiber filter paper by an acid mist sampling train. Sulfates are determined turbidimetrically by the formation of barium sulfate as barium chloride is added. The absorbance of the barium sulfate suspension is measured spectrophotometrically at 500 mμ with a 1-inch cell path. This method is applicable for the determination of sulfate ion concentrations of from 0 to 50 μg/ml in aqueous media.

Reagents

All chemicals must be ACS analytical reagent grade.

Water

Deionized or distilled water.

Absorbing Reagent

Hydrogen peroxide (3 percent) – Dilute 10 ml of 30 percent hydrogen peroxide to 100 ml.

Sulfa Ver Powder

For sulfates in water manufactured by the Hack Chemical Company, Ames, Iowa.*

Standard Sodium Sulfate

Dissolve 1.469 grams of sodium sulfate in 1 liter of water. Dilute 100.0 ml of this solution to 1 liter with water in a volumetric flask. This solution contains 100 μg (SO_4^-)/ml.

Sample Preparation

Transfer the contents of the midget impingers or the glass fiber filter to a sample container. Dilute the impinger solution to a known volume and/or add a known volume of water to the filter for solubalization of the sulfate.

Procedure

Pipet 20 ml or a suitable aliquot made up to 20 ml into a 1-inch cuvette or test tube. Read the absorbance against a distilled water blank (blank correction). This value will be subtracted from the final absorbance reading to correct for unmatched cuvettes. Add one level spoonful (0.3 g) of Sulfa Ver powder and shake to mix.

Between 5 minutes and 20 minutes after the Sulfa Ver powder is added, the absorbance should be read on a spectrophotometer at 500 mμ. Use a blank of

*Mention of company or product name does not constitute endorsement by the U.S. Department of Health, Education, and Welfare.

water and Sulfa Ver powder to set the spectrophotometer to zero absorbance. Determine the amount of sulfate present from a previously prepared calibration curve.

Preparation of Calibration Curve

Prepare a series of standards ranging from 0 to 50 μg/ml from the working standards solution. Measure the absorbance of these standard solutions in the manner described in the procedure. Construct a calibration curve by plotting $\mu g\,(SO_4)$/ml versus absorbance.

Calculations

Compute the number of mg of SO_2 present in the sample by the following formula:

$$SO_2, \text{mg} = (SO_4^-)\ \text{mg} \times \frac{64}{96}$$

64 = molecular weight of SO_2
96 = molecular weight of (SO_4^-)

Compute mg of H_2SO_4 present in the sample by the following formula:

$$H_2SO_4, \text{mg} = (SO_4^-), \text{mg} \times \frac{98}{96}$$

96 = molecular weight of (SO_4^-)
98 = molecular weight of sulfuric acid.

$$SO_2, \text{ppm} = \frac{(377)(\text{mg of } SO_2)}{V_s}$$

377 = μl/mg of SO_2 at 70° F and 29.92 inches of Hg
V_s = volume of gas sampled in liters at 70° F and 29.92 inches of Hg

$$H_2SO_4, \mu g/m^3 = \frac{H_2SO_4, \mu g}{V_s}$$

V_s = volume of gas sampled in cubic meters at 70° F and 29.92 inches of Hg

APPENDIX B. HYDROCHLORIC ACID MANUFACTURING ESTABLISHMENTS LOCATED IN UNITED STATES

January 1968

Type of Process Utilized

B = By-Product
S = Chlorine-Hydrogen Synthesis
M = Mannheim
H = Hargreaves

State	Company name	Location	Type
Alabama			
	Giegy Chemical Corp.	McIntosh	B
	Monsanto Co.	Anniston	B
	Olin Matheison Chemical Corp.	McIntosh	B
	Olin Matheison Chemical Corp.	Huntsville	B
	Stauffer Chemical	LeMoyne	B
Arkansas			
	Arkla Chemical Corp.	Pine Bluff	S
California			
	American Chemical Corp.	Long Beach	B
	J.H. Baxter & Company	Long Beach	B
	Chevron Chemical Company	Richmond	B
	Dow Chemical Co.	Pittsburgh	B
	E.I. duPont deNemours & Co.	Antioch	B
	Neville Chemical Co.	Santa Fe Springs	B
	Stauffer Chemical Co.	Dominguez (L.A.)	B
	Montrose Chemical Corp. of Calif.	Torrance	B
	Witfield Chemical Corp.	Watson	B
Connecticut			
	The Upjohn Co.	North Haven	B
	Uniroyal Co.	Naugatuck	B
Delaware			
	Allied Chemical Corp.	North Claymont	B
	Standard Chlorine of Delaware	Delaware City	B

Georgia		
Chemical Products Corp.	Cartersville	B
Hercules, Inc.	Brunswick	B
Merck & Company	Albany	B
Illinois		
Allied Chemical Corp.	Danville	B
Baird Chemical Industries, Inc.	Peoria	B
Cabot Corp.	Tuscola	B
Monsanto Co.	Sauget	B
The Richardson Co.	Chicago	B
The Richardson Co.	Lemont	B
Indiana		
E.I. duPont deNemours & Co.	East Chicago	B
Keil Chemical	Hammond	B
Kansas		
Racon, Inc.	Clearwater	B
Vulcan Materials Co.	Wichita	B,S
Kentucky		
E.I. duPont deNemours & Co.	Louisville	B
Hooker Chemical Corp.	South Shore	B
Pennsalt Chemical Corp.	Calvert City	B
Stauffer Chemical Co.	Louisville	B
Louisiana		
Allied Chemical Corp.	Geismar	B
Allied Chemical Corp.	Baton Rouge	B
Conoco	Lake Charles	B
Dow Chemical Co.	Plaquemine	B,S
Ethyl Corp.	Baton Rouge	B,S
Hooker Chemical Co.	Taft	B
Kaiser Aluminum & Chemical Co.	Gramercy	B
Morton Chemical Co.	Weeks Island	H
Morton Chemical Co.	Giesmar	B
Pittsburgh Plate Glass Co.	Lake Charles	B
Rubicon Chemicals, Inc.	Lake Charles	B
Shell Chemical Co.	Norco	B
Vulcan Materials Co.	Geismar	B
Wyandotte Chemical Corp.	Geismar	B
Maryland		
Chemetron Corp.	Elkton	B
Continental Oil Co.	Baltimore	B
FMC	Baltimore	B

Massachusetts		
Monsanto Co.	Everett	B
Solvent Chemical Co.	Malden	B
Michigan		
Dow Chemical Co.	Midland	B
Dow Corning Co.	Midland	B
E.I. duPont deNemours & Co.	Montague	B
Hooker Chemical Corp.	Montague	S
Ott Chemical Corp.	Muskegon	B
Pennsalt Chemical Corp.	Wyandotte	B,S
Missouri		
Monsanto	St. Louis	B
Nevada		
Montrose Chemical Corp. of Calif.	Henderson	B
Stauffer Chemical Co.	Henderson	B
New Jersey		
Allied Chemical Corp.	Elizabeth	B
Baldwin-Montrose Calif. Co.	Newark	B
Benzol Products Div.	Newark	B
W.A. Cleary Corp.	New Brunswick	B
Diamond Alkali Co.	Newark	B
E.I. duPont deNemours & Co.	Carney's Point	B
E.I. duPont deNemours & Co.	Deepwater	B
E.I. duPont deNemours & Co.	Linden	M
Enjay Chemical Co.	Bayway	B
General Aniline & Film Corp.	Linden	S
Hercules, Inc.	Parlin	B
ICI	Bayonne	B
Merck & Co.	Rahway	B
Mobil Oil Corp.	Metuchen	B
Pearsall Chemical Corp.	Phillipsburg	B
Tenneco Chemical Inc.	Fords	B
Toms River Chemical Corp.	Toms River	B
Vulcan Materials Co.	Newark	B
Weston Chemicals Corp.	Newark	B
White Chemicals Co.	Bayonne	B
New Mexico		
Climax Chemical Co.	Hobbs	M
New York		
Allied Chemical Corp.	Buffalo	B
Allied Chemical Corp.	Syracuse	B
E.I. duPont deNemours & Co.	Niagra Falls	B,S

Eastman Kodak Co.	Rochester	B
Hooker Chemical Corp.	Niagra Falls	B,S
Hooker Chemical Corp.	North Tonawanda	B,S
Stauffer Chemical Corp.	Niagra Falls	B
Ohio		
Detrex Chemical Ind.	Ashtabula	B
Diamond Alkali Co.	Painesville	B,S
Dover Chemical Corp.	Dover	B
E.I. duPont deNemours & Co.	Cleveland	M
Olin Matheison Chemical Corp.	Ashtabula	B
Pittsburgh Plate Glass Co.	Barberton	B
Tennessee Corp.	Evendale	M
Oregon		
Pennsalt Chemical Corp.	Portland	S
Pennsylvania		
Allegheny Electronic Chemical Co.	Bradford	B
Koppers Co., Inc.	Bridgeville	B
Lebanon Chemical Co.	Lebanon	B
Rohm & Haas Co.	Philadelphia	B
U.S. Steel Corp.	Clairton	B
Tennessee		
Stauffer Chemical Co.	Mt. Pleasant	B
Velsicol Chemical Corp.	Chattanooga	B
Texas		
Atlantic Richfield Co.	Port Arthur	B
Diamond Alkali Co.	Deer Park	B,S
Diamond Alkali Co.	Greens Bayou	B
Dow Chemical Co.	Freeport	B
Dow Chemical Co.	Oyster Creek	B
E.I. duPont deNemours & Co.	La Porte	S
Ethyl Corp.	Houston	B,S
Monsanto Co.	Texas City	B
Monsanto Co.	Alvin	B
Phillips Petroleum Co.	Pasadena	B
Phillips Petroleum Co.	Deer Park	B
Potash Co. of America	Dumus	B
Shell Chemical Co.	Houston	B
Stauffer Chemical Co.	Fort Worth	M
Union Carbide Corp.	Texas City	B
The Upjohn Co.	La Porte	B
Vulcan Materials Co.	Denver City	S

Utah			
	National Lead Co.	Lakepoint	(experimental)
Virginia			
	Hercules, Inc.	Hopewell	M
	Olin Matheison Chemical Corp.	Saltville	S
Washington			
	Hooker Chemical Corp.	Tacoma	S,B
	Pennsalt Chemical Corp.	Tacoma	S
	Reichhold Chemicals, Inc.	Tacoma	B
West Virginia			
	Allied Chemical Corp.	Moundsville	B
	Diamond Alkali Co.	Belle	B
	FMC Corp.	South Charleston	B
	FMC Corp.	Nitro	B
	Mobay Chemical Co.	New Martinsville	B
	Monsanto Co.	Nitro	B
	Pittsburgh Plate Glass Co.	Natrium	B,S
	Stauffer Chemical Co.	Gallipolis Ferry	B
	Union Carbide Corp.	Institute	B
	Union Carbide Corp.	South Charleston	B

APPENDIX C.
PHYSICAL DATA–HYDROCHLORIC ACID

Table C-1. SPECIFIC GRAVITIES OF AQUEOUS HYDROCHLORIC ACID SOLUTIONS[a]

Standard Adopted 1903
Authority – W. C. Ferguson

Density, ° Bé	Specific gravity	Percent HCl	Density, ° Bé	Specific gravity	Percent HCl	Density, ° Bé	Specific gravity	Percent HCl
1.00	1.0069	1.40	16.0	1.1240	24.57	20.8	1.1675	32.93
2.00	1.0140	2.82	16.1	1.1248	24.73	20.9	1.1684	33.12
3.00	1.0211	4.25	16.2	1.1256	24.90	21.0	1.1694	33.31
4.00	1.0284	5.69	16.3	1,1265	25.06	21.1	1.1703	33.50
5.00	1.0357	7.15	16.4	1.1274	25.23	21.2	1.1713	33.69
5.25	1.0375	7.52	16.5	1.1283	25.39	21.3	1.1722	33.88
5.50	1.0394	7.89	16.6	1.1292	25.56	21.4	1.1732	34.07
5.75	1.0413	8.26	16.7	1.1301	25.72	21.5	1.1741	34.26
6.00	1.0432	8.64	16.8	1.1310	25.89	21.6	1.1751	34.45
6.25	1.0450	9.02	16.9	1.1319	26.05	21.7	1.1760	34.64
6.50	1.0469	9.40	17.0	1.1328	26.22	21.8	1.1770	34.83
6.75	1.0488	9.78	17.1	1.1336	26.39	21.9	1.1779	35.02
7.00	1.0507	10.17	17.2	1.1345	26.56	22.0	1.1789	35.21
7.25	1.0526	10.55	17.3	1.1354	26.73	22.1	1.1798	35.40
7.50	1.0545	10.94	17.4	1.1363	26.90	22.2	1.1808	35.59
7.75	1.0564	11.32	17.5	1.1372	27.07	22.3	1.1817	35.78
8.00	1.0584	11.71	17.6	1.1381	27.24	22.4	1.1827	35.97
8.25	1.0603	12.09	17.7	1.1390	27.41	22.5	1.1836	36.16
8.50	1.0623	12.48	17.8	1.1399	27.58	22.6	1.1846	36.35
8.75	1.0642	12.87	17.9	1.1408	27.75	22.7	1.1856	36.54
9.00	1.0662	13.26	18.0	1.1417	27.92	22.8	1.1866	36.73
9.25	1.0681	13.65	18.1	1.1426	28.09	22.9	1.1875	36.93
9.50	1.0701	14.04	18.2	1.1435	28.26	23.0	1.1885	37.14
9.75	1.0721	14.43	18.3	1.1444	28.44	23.1	1.1895	37.36
10.00	1.0741	14.83	18.4	1.1453	28.61	23.2	1.1904	37.58
10.25	1.0761	15.22	18.5	1.1462	28.78	23.3	1.1914	37.80
10.50	1.0781	15.62	18.6	1.1471	28.95	23.4	1.1924	38.03
10.75	1.0801	16.01	18.7	1.1480	29.13	23.5	1.1934	38.26
11.00	1.0821	16.41	18.8	1.1489	29.30	23.6	1.1944	38.49
11.25	1.0841	16.81	18.9	1.1498	29.48	23.7	1.1953	38.72
11.50	1.0861	17.21	19.0	1.1508	29.65	23.8	1.1963	38.95
11.75	1.0881	17.61	19.1	1.1517	29.83	23.9	1.1973	39.18
12.00	1.0902	18.01	19.2	1.1526	30.00	24.0	1.1983	39.41
12.25	1.0922	18.41	19.3	1.1535	30.18	24.1	1.1993	39.64
12.50	1.0943	18.82	19.4	1.1544	30.35	24.2	1.2003	39.86
12.75	1.0964	19.22	19.5	1.1554	30.53	24.3	1.2013	40.09
13.00	1.0985	19.63	19.6	1.1563	30.71	24.4	1.2023	40.32
13.25	1.1006	20.04	19.7	1.1572	30.90	24.5	1.2033	40.55
13.50	1.1027	20.45	19.8	1.1581	31.08	24.6	1.2043	40.78
13.75	1.1048	20.86	19.9	1.1590	31.27	24.7	1.2053	41.01
14.00	1.1069	21.27	20.0	1.1600	31.45	24.8	1.2063	41.24
14.25	1.1090	21.68	20.1	1.1609	31.64	24.9	1.2073	41.48
14.50	1.1111	22.09	20.2	1.1619	31.82	25.0	1.2083	41.72
14.75	1.1132	22.50	20.3	1.1628	32.01	25.1	1.2093	41.99
15.00	1.1154	22.92	20.4	1.1637	32.19	25.2	1.2103	42.30
15.25	1.1176	23.33	20.5	1.1647	32.38	25.3	1.2114	42.64
15.50	1.1197	23.75	20.6	1.1656	32.56	25.4	1.2124	43.01
15.75	1.1219	24.16	20.7	1.1666	32.75	25.5	1.2134	43.40

Allowance for temperature:

10-15° Bé. 1/40° Bé or 0.0002 Sp. Gr. for 1° F.
10-22° Bé. – 1/30° Bé or 0.0003 Sp. Gr. for 1° F.
22-25° Bé. – 1/28° Bé or 0.00035 Sp. Gr. for 1° F.

[a]Originally published as Manufacturing Chemists' Association, Inc. Manual Sheet SD-39. Copies of a similar table giving ° Bé, Sp. Gr. and Tw ° corresponding with percent HCl, are available through the MCA as Manual Sheet T-3.

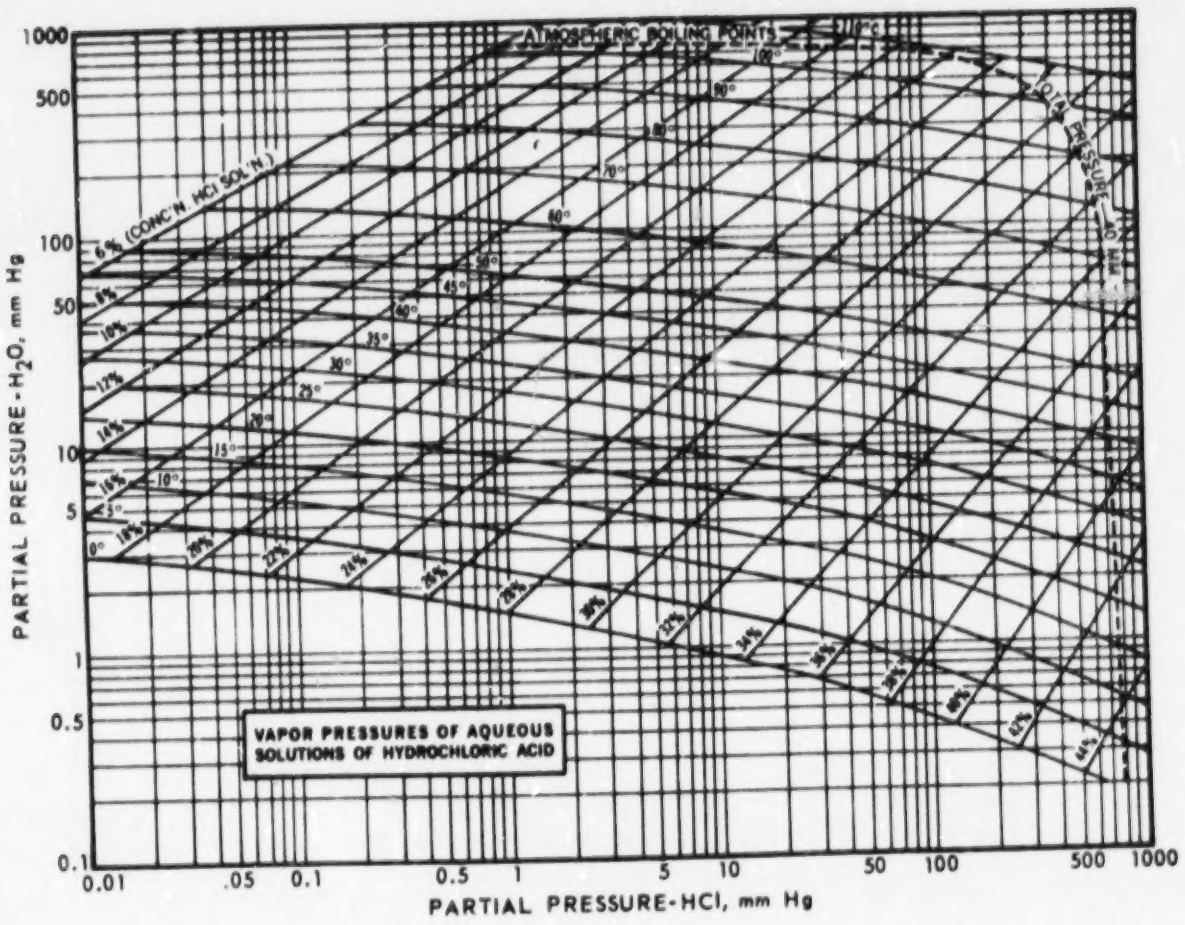


Figure C-1. Vapor pressure of hydrochloric acid at various concentrations.

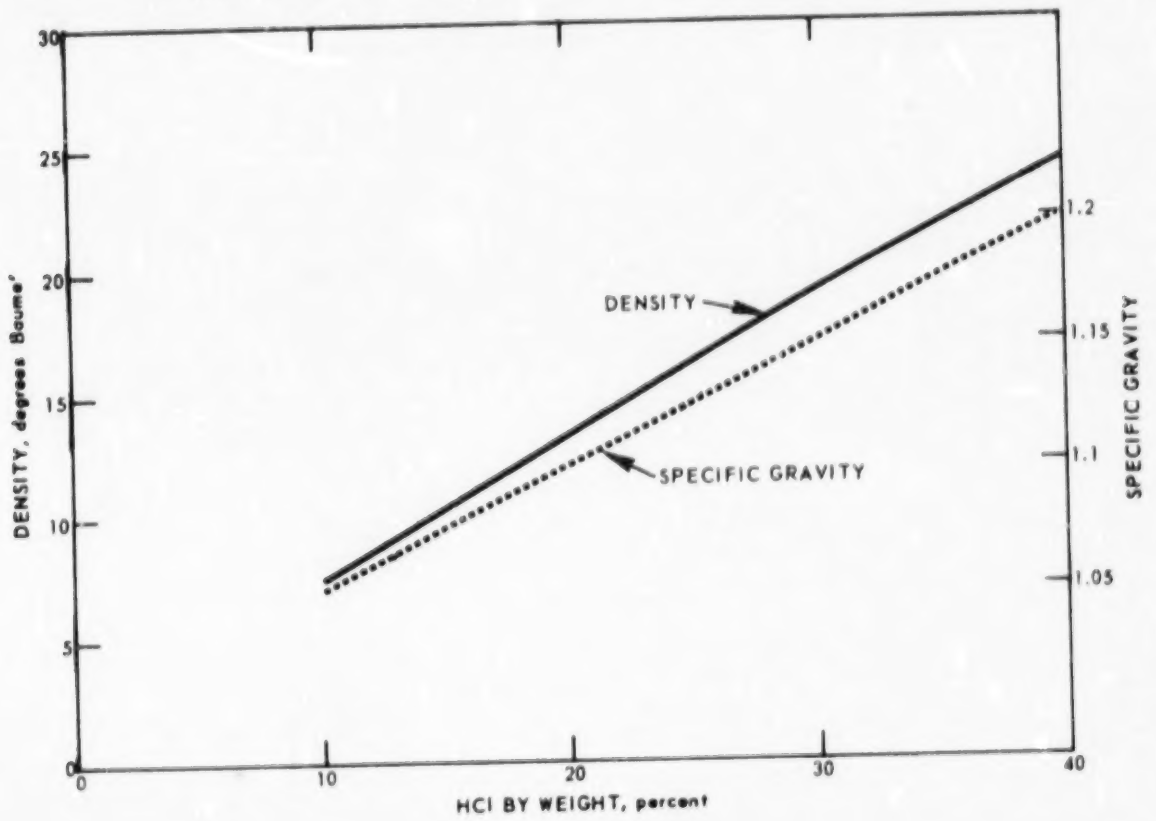


Figure C-2. Specific gravity and density versus percent hydrogen chloride.

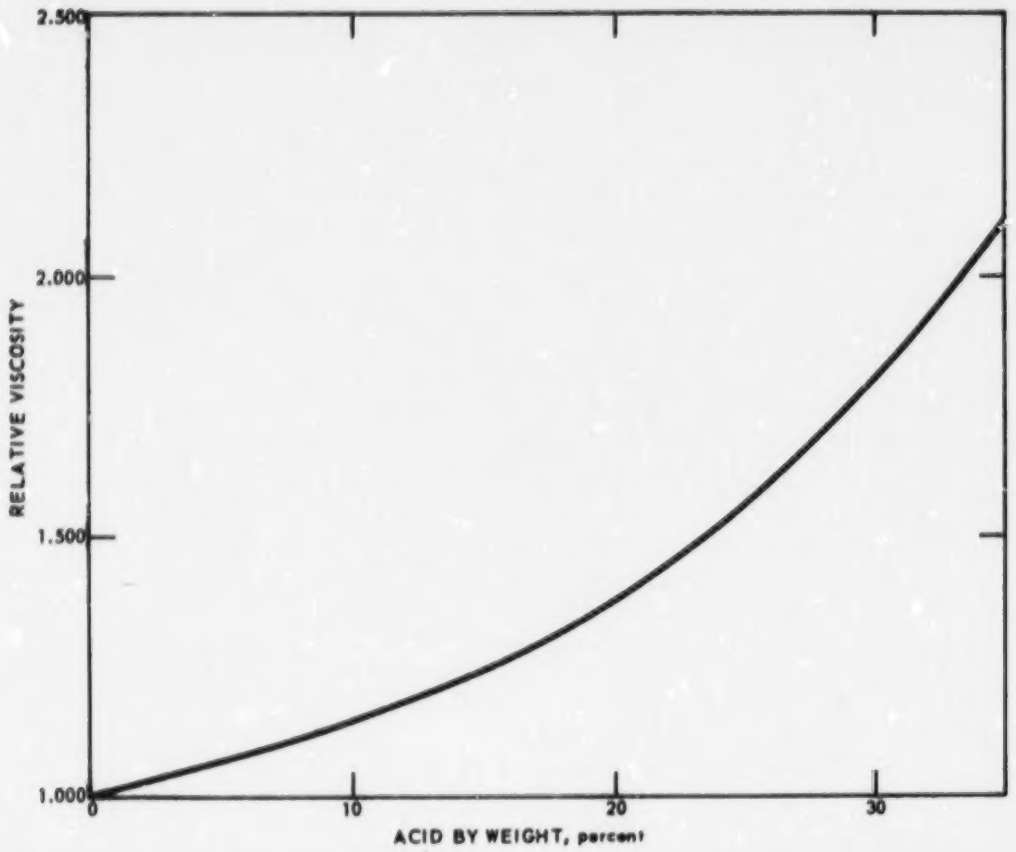


Figure C-3. Relationship of viscosities of hydrogen chloride and water.

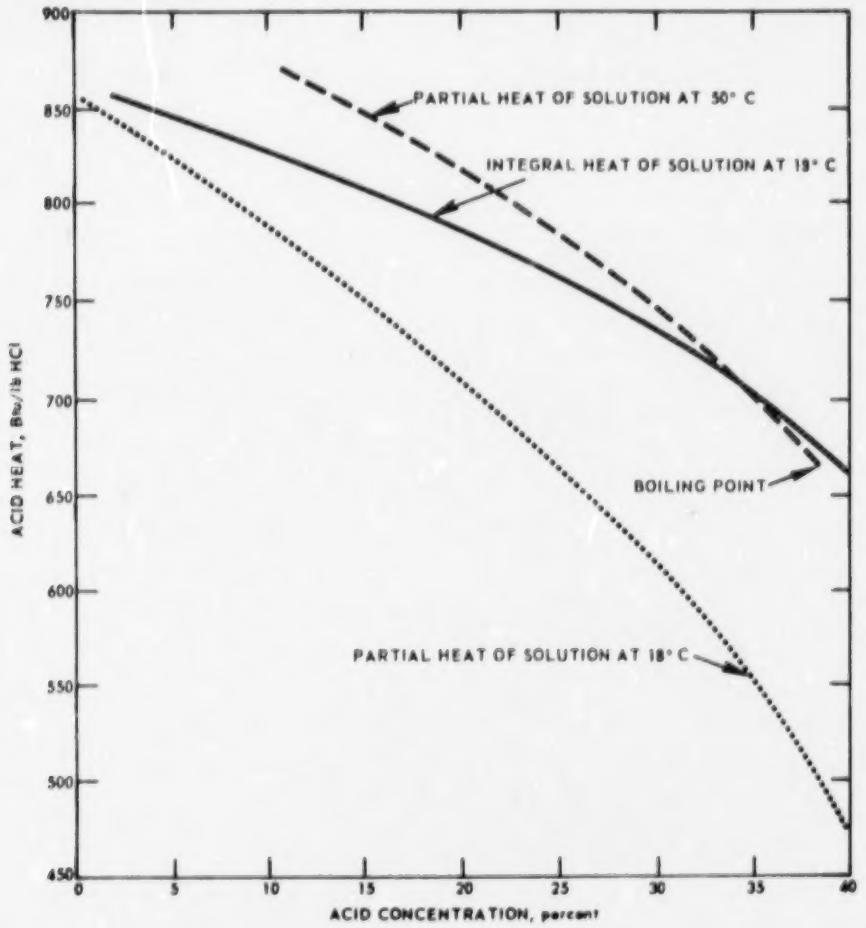


Figure C-4. Heats of solution of hydrogen chloride in water.

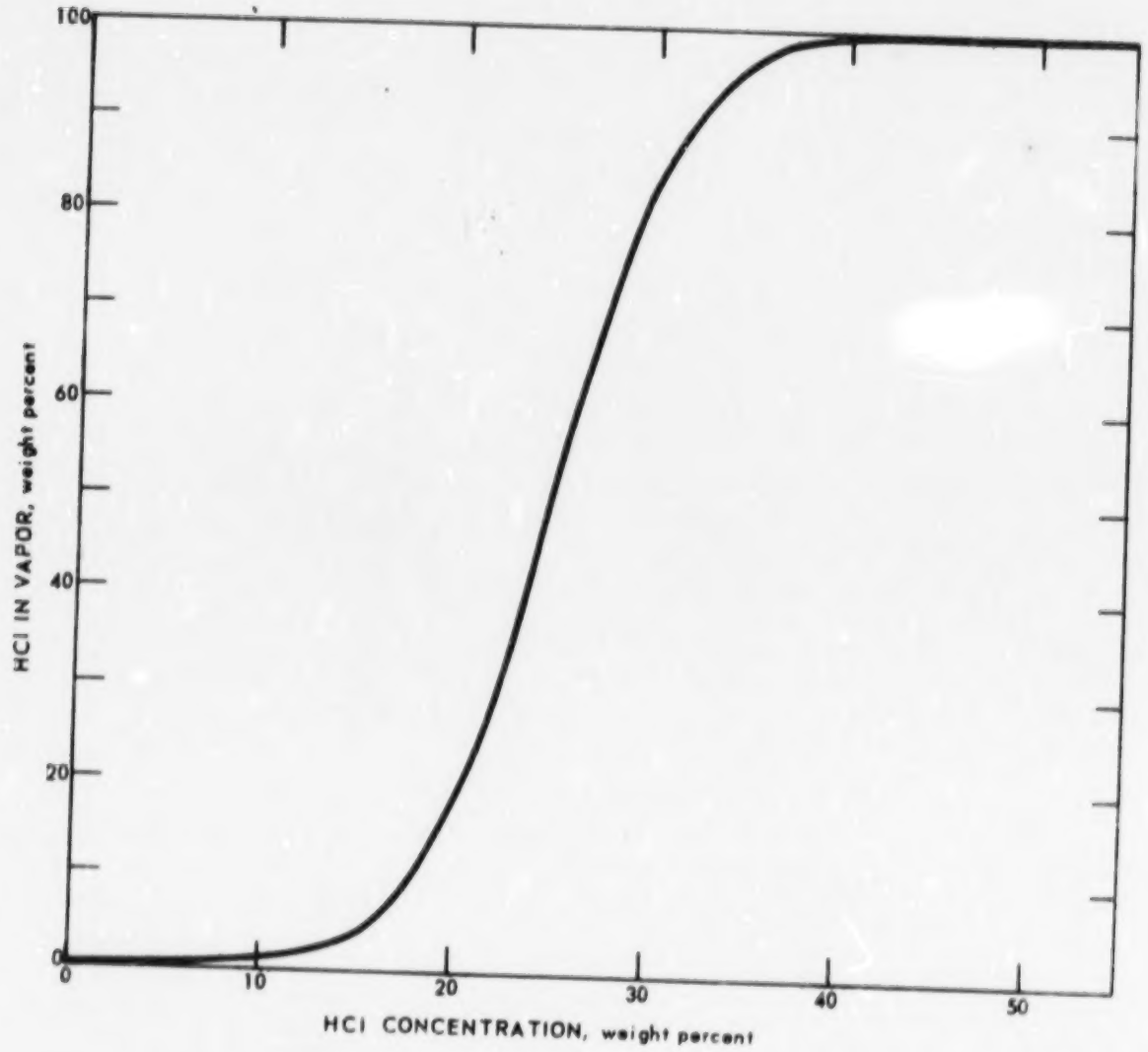


Figure C-5. Vapor-liquid equilibra for hydrochloric acid.

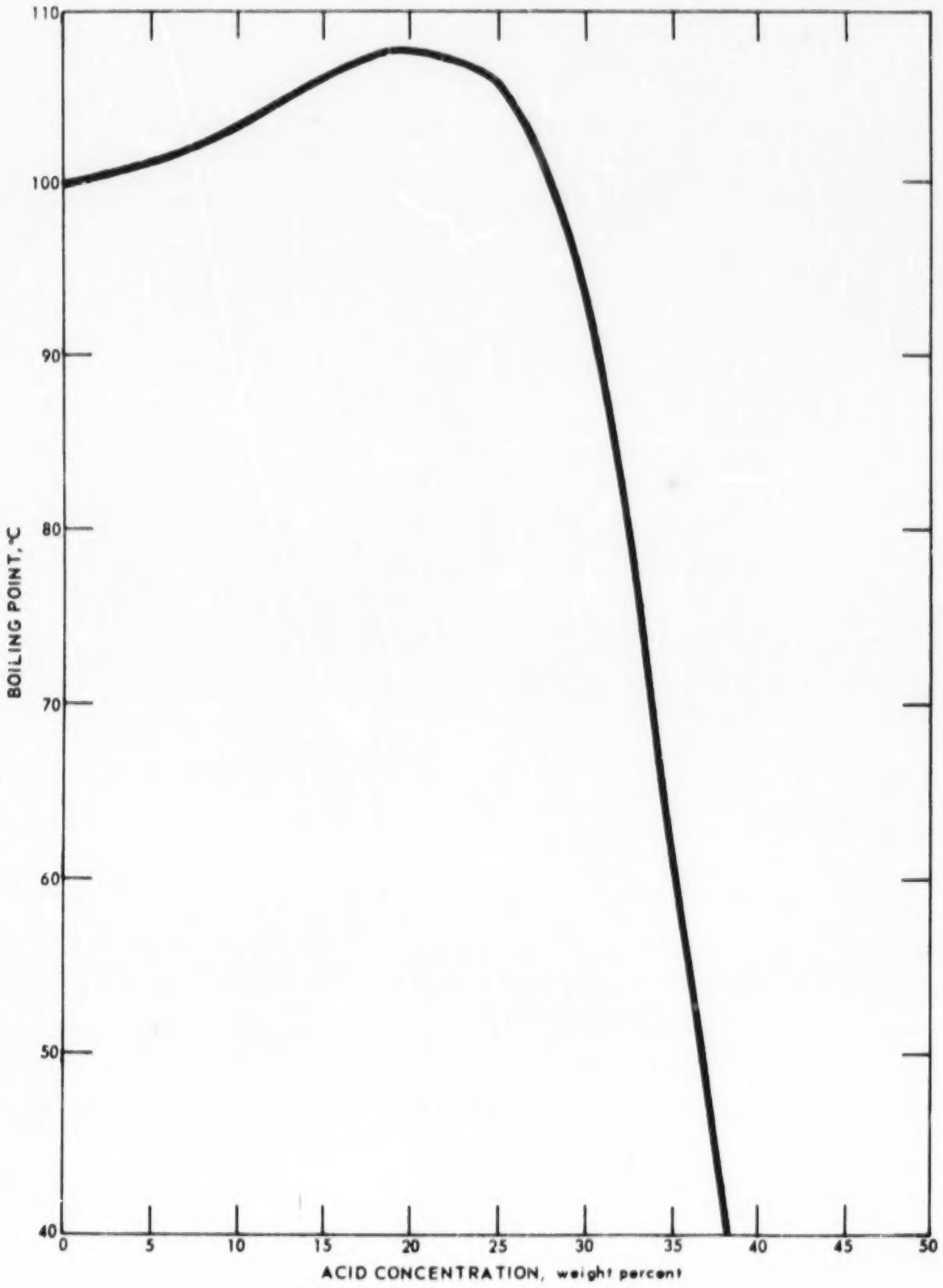


Figure C-6. Boiling point of hydrochloric acid solution.

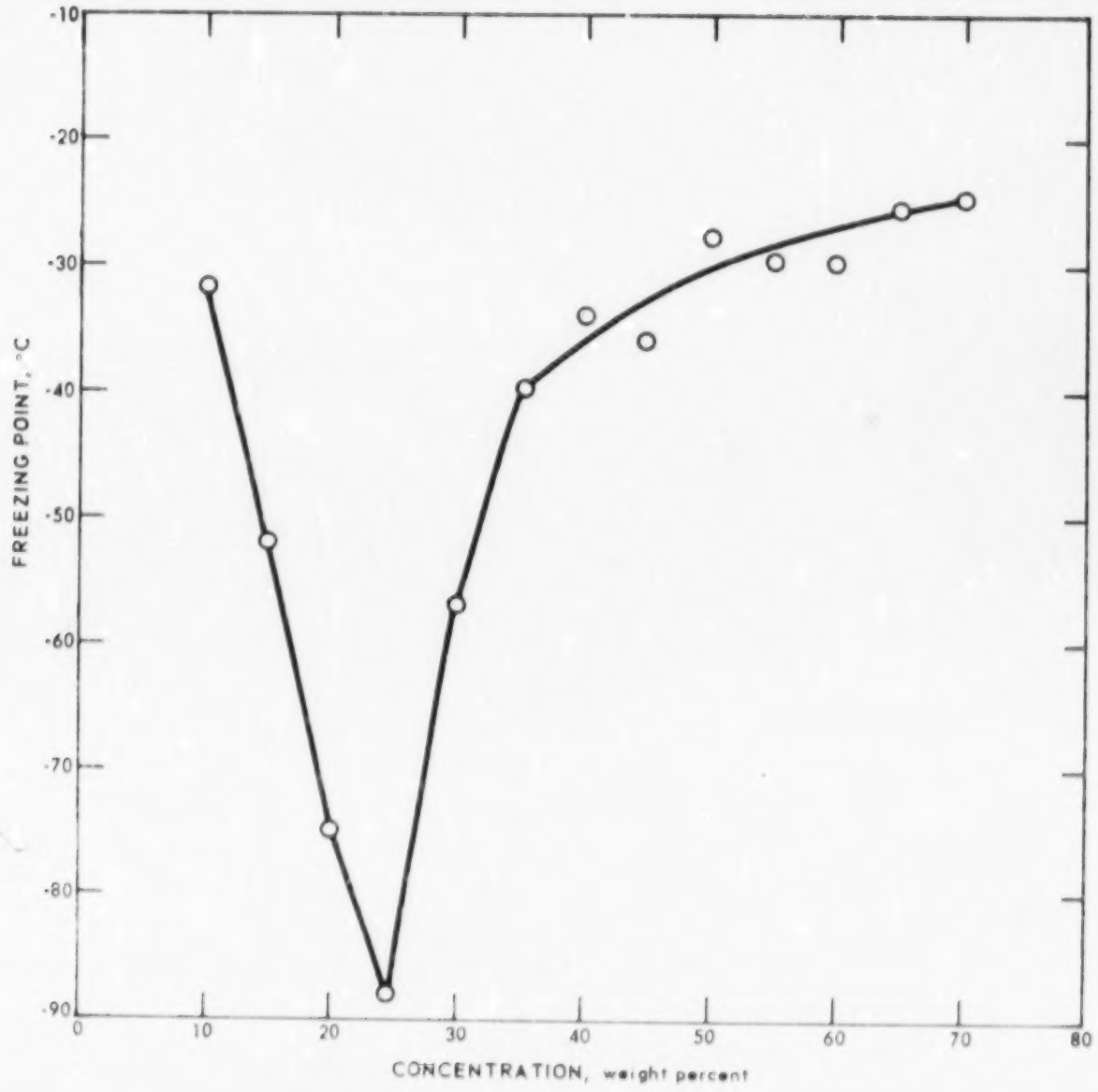


Figure C-7. Freezing point of aqueous hydrogen chloride.

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